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Journal

ACS Catalysis, 10(8)

ISSN

2155-5435

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Publication Date

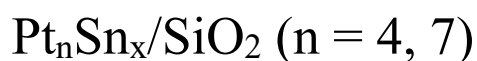
2020-04-17

DOI

10.1021/acscatal.0c00668

Peer reviewed

Coking-Resistant Sub-Nano Dehydrogenation Catalysts:



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ABSTRACT

We present a combined experimental/theoretical study of Pt_n/SiO_2 and $\text{Pt}_n\text{Sn}_x/\text{SiO}_2$ ($n = 4, 7$) model catalysts for the endothermic dehydrogenation of hydrocarbons, using the ethylene intermediate as a model reactant. Mass-selected Pt_n clusters were deposited onto amorphous $\text{SiO}_2/\text{Si}(100)$ to make the Pt_nSiO_2 model catalysts. To produce Pt_nSn_x clusters, size-selected Pt_n were used to seed selective deposition of Sn on Pt via a self-limiting $\text{H}_2/\text{SnCl}_4/\text{H}_2$ reaction sequence. Model catalysts were analyzed using C_2D_4 and CO temperature programmed desorption (TPD), low energy ion scattering (ISS), X-ray photoelectron spectroscopy (XPS), plane wave density functional theory (DFT) global optimization combined with a statistical mechanical description of the catalytic interface, and a DFT mechanistic study. Supported pure Pt_n clusters are found to be highly active toward dehydrogenation of C_2D_4 , quickly deactivating due to a combination of carbon deposition and sintering, resulting in loss of accessible Pt sites. Addition of Sn to Pt_n clusters results in the complete suppression of C_2D_4 dehydrogenation and carbon deposition, and also stabilizes the clusters against thermal sintering. Theory shows that both systems have thermal access to a multitude of cluster structures and adsorbate configurations that form a statistical ensemble. While Pt_4/SiO_2 clusters bind ethylene in both di- σ - and π -bonded configurations, $\text{Pt}_4\text{Sn}_3/\text{SiO}_2$ binds C_2H_4 only in the π -mode, with di- σ bonding suppressed by a combination of electronic and geometric features of the PtSn clusters. Dehydrogenation reaction profiles on the accessible cluster isomers were calculated using the climbing image nudged elastic band (CI-NEB) method. Dehydrogenation of di- σ bound ethylene is computed to dominant, and suppressed by Sn addition, in agreement with the experiments. DFT indicates that after Sn alloying, the barrier for ethane-to-ethylene conversion is lower than that for unwanted ethylene dehydrogenation.

KEYWORDS: dehydrogenation, cluster catalysis, fluxionality, coking, PtSn

INTRODUCTION

Carbon deposition (“coking”) in high temperature reactions under hydrocarbon-rich conditions is a serious catalyst deactivation mechanism, thus understanding the mechanism and developing approaches to suppress carbon deposition are interesting. One reaction of this type is endothermic alkane dehydrogenation, and we have been examining carbon deposition over sub-nano Pt¹ and Pt alloy cluster catalysts,²⁻⁴ with the goal of stabilizing the clusters against both coking and sintering, which is a serious problem for clusters at high temperatures. In addition to maximizing the accessibility of precious metal atoms in the surface layer, sub-nano clusters often have size-dependent properties that provide additional opportunities for catalyst tuning.⁵⁻¹⁵ Small clusters are also relatively tractable theoretically, thus these systems allow detailed modeling of the effects of cluster physical and chemical properties on reaction mechanisms.^{9, 16-22} Even for a single cluster size, however, cluster reactions can be quite complex, with multiple structural isomers contributing and evolving during reactions due to thermal and adsorbate effects.

Because reducing coking on Pt-based catalysts is important in many applications, there have been many studies of mitigation strategies. Here we focus on use of Pt-Sn alloy catalysts for dehydrogenation and other reactions where coking is problematic. For example, coke formation has been studied on practical Pt catalysts²³⁻²⁴ and has been addressed by passivating specific metal sites with Sn, ranging from trace to stoichiometric amounts.²⁵⁻³⁰ Though successful, the complex nature of practical catalysts makes detailed understanding of the mechanistic origins of the Pt-Sn relationship and its beneficial effects on catalytic dehydrogenation difficult. It is useful, therefore, to consider model catalysts, including ordered surface alloys and planar supported cluster catalysts.

Koel and co-workers studied the branching between alkene desorption and decomposition/dehydrogenation (leading to carbon deposition) on a series of ordered Pt-Sn surface

alloys, ranging from pure Pt(111) to an alloy with 2:1 Pt:Sn stoichiometry. With increasing Sn content, the desorption temperature for the alkenes decreased substantially, without any reduction in the saturation coverage. By decreasing the binding energy, desorption of intact alkenes becomes favored over further dehydrogenation. (i.e., coking is suppressed). It was found that the di- σ ethylene binding geometry was preferred for all the alloys, as well as for Pt (111).³¹⁻³² In a comparable study using DFT methods, ethane adsorption to extended Pt and PtSn surfaces was explored by Hook *et al.*, who also found that ethylene binds in a di- σ fashion to both Pt and PtSn extended surfaces. As in the experiments, the ethylene adsorption energy decreased below the barrier for dehydrogenation of ethylene, resulting in suppression of dehydrogenation and carbon deposition.³³ This was rationalized as being due to a combination of binding geometry and electronic effects.

For small PtSn supported nanoparticles, some differences have been noted. For example, Shen *et al.*³⁰ and Natal-Santiago *et al.*²⁹ studied adsorption geometries and energies of ethylene to silica-supported Pt and PtSn catalyst particles (diam. = 2-5 nm) using microcalorimetry and IR spectroscopy. The nano Pt catalyst supported both di- σ and π -bound ethylene, and incorporation of Sn resulted in a decrease in the heat of adsorption and an increase in the fraction of π -bound ethylene with increasing Sn content. The appearance of substantial π -bonding for small PtSn nanoparticles differs from the observation of purely di- σ bonding for extended PtSn surface alloys, suggesting significant effects of particle size. Sub-nanometer, or “ultra-dispersed” catalysts would therefore be expected to have additional differences in catalytic behavior. For example, in a study of propane dehydrogenation, Datye *et al.*, examined 0.6 ± 0.2 nm Pt and PtSn particles on Al₂O₃.³⁴ From a thermal stability perspective, it was proposed that Sn helped maintain the dispersion of Pt

particles under reaction and oxidative regeneration conditions, and that this was the major contributor to the prolonged activity for PtSn vs. pure Pt catalysts.

In another study with sub-nanometer particles, Ha and Baxter *et al.*¹⁴ added boron to size-selected Pt_n/Al₂O₃ model catalysts to suppress dehydrogenation/coking during ethylene temperature-programmed desorption/reaction (TPD/R). The model catalyst was well-defined enough to allow an accurate DFT model to be built and used to examine changes in energetics and mechanisms for ethylene binding/desorption from Pt_n/Al₂O₃¹ and Pt_nB_x/Al₂O₃.³ Addition of boron suppressed di-σ binding of ethylene, and substantially lowered the desorption energy, such that ethylene desorbed rather than undergoing dehydrogenation leading to carbon deposition.

Here we apply size-selection methods to study PtSn/SiO₂ model catalysts. Size- and composition-selected clusters were prepared by using mass-selected Pt_n deposition to prepare planar SiO₂ supports decorated by a precisely controlled coverage of size-selected clusters. These were then used to seed highly selective Sn deposition on the clusters via a self-limiting reaction process. The composition and morphology were probed using X-ray photoelectron and low-energy ion scattering spectroscopies (XPS, ISS). Pt_n/SiO₂ was chosen as the system, because the process used to deposit Sn is quite selective, depositing Sn almost exclusively on the Pt clusters, rather than on the SiO₂ support. We initially examined Sn modification of Pt_n/alumina/NiAl(110) and Pt_n/alumina/Ta(110), but found considerable non-selective Sn deposition on the alumina supports. Those systems have interesting catalytic activity,³⁵ but for the purpose of studying Pt_nSn_x clusters with well-defined composition, the SiO₂ support is better. Additional detail on catalyst preparation is available below in the Methods section, and a complete characterization of stoichiometry, size, and composition has been previously published.² Here, we compare catalytic properties of Pt₄/SiO₂ and Pt₇/SiO₂ to these size- and composition-controlled Pt₄Sn_{3.3}/SiO₂ and

Pt₇Sn_{6.3}/SiO₂ bimetallic cluster catalysts. DFT calculations are used to examine structure and binding properties of the clusters for thermally populated cluster isomer ensembles for Pt₄/SiO₂ and Pt₄Sn₃/SiO₂. Note that the amorphous structure of the SiO₂ native oxide requires a large slab in the calculations. This factor, together with the need to consider the thermally accessible isomer ensembles, makes the DFT calculations quite expensive even for small Pt_nSn_x/SiO₂, and infeasible for larger clusters.

RESULTS AND DISCUSSION

In the following, we present experiments comparing Pt_n/SiO₂ and Pt_nSn_x/SiO₂, for four clusters: Pt₄, Pt₇, Pt₄Sn_{3.3}, and Pt₇Sn_{6.3}. The theory results are focused on Pt₄/SiO₂ and Pt₄Sn₃/SiO₂, however, the experiments for Pt₄ and Pt₇ suggest that similar considerations should apply to the Pt₇ and Pt₇Sn_{6.3} experiments. The two Pt_n cluster sizes were selected because Pt₄ and Pt₇ had been studied previously on Al₂O₃ supports, with Pt₄ found to have all atoms exposed in the surface layer and Pt₇ having both single layer and prismatic 3D isomers, the latter of which was found to isomerize to a single layer structure upon adsorption of multiple ethylene molecules.¹ In addition, the low energy structures for Pt₄Sn₃/SiO₂ were already available from our paper describing the method for producing size- and composition-selected Pt_nSn_x/SiO₂ model catalysts.²

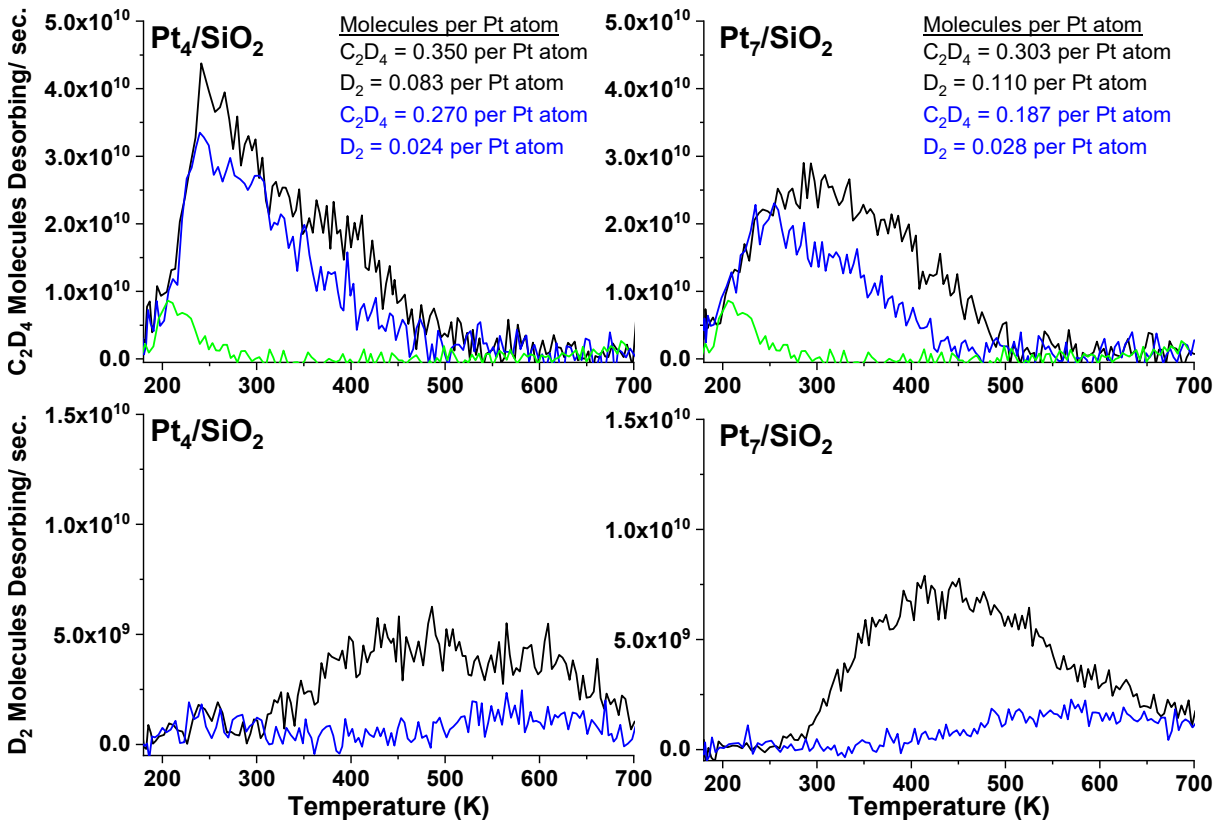


Figure 1. Intact desorption of C_2D_4 (top) and D_2 (bottom) from the first (black) and fourth (blue) C_2D_4 TPD. These spectra were collected after a 10 L dose of C_2D_4 to Pt_n/SiO_2 ($n = 4, 7$). C_2D_4 desorption from SiO_2 is also plotted (green), no D_2 evolution from SiO_2 is observed.

Ethylene Desorption vs. Dehydrogenation. C_2D_4 and D_2 desorption from Pt_4/SiO_2 and Pt_7/SiO_2 are shown in **Fig. 1**. To examine the effects of repeated C_2D_4 exposure and heating, a total of four TPD/R runs were carried out, but the figure shows results only for the 1st (black) and 4th (blue) runs. The data for all four runs are shown in **Fig. S1**. Most experiments were done with C_2D_4 to avoid interference with H_2 detection from high background at mass 2, however, the background is also high at mass 28, corresponding to C_2D_2 . Therefore, some experiments were done using C_2H_4 to look for acetylene desorption. None was observed. We also looked for ethane signal from possible hydrogenation processes, but the signals were negligible. Because cracking

of C_2D_4 to D_2^+ in the mass spectrometer is weak, this contribution to the D_2 signal has not been subtracted in the figure.

The figures also show the C_2D_4 desorption observed from a Pt-free SiO_2 substrate (green), indicating that for the 180 K C_2D_4 exposure temperature chosen, only a small amount of C_2D_4 desorbs from the SiO_2 substrate, and that SiO_2 does not support D_2 desorption. We tested the effect of lowering the dose temperature from 180 K to 150 K, observing a large increase in the desorption intensity from the SiO_2 support. The integrated C_2D_4 TPD signal after 180 K dosing on SiO_2 corresponds to $\sim 3.5 \times 10^{12}$ molecules/ cm^2 – well below 1% of a monolayer.

For Pt_n/SiO_2 samples, C_2D_4 desorption also begins at 180 K, initially matching the desorption from SiO_2 , but then continuing with much higher intensities before eventually declining and disappearing by ~ 500 K. The signal between 180 K and ~ 220 K is, therefore, attributed to desorption mostly from SiO_2 sites, while the signal at higher temperatures is attributed to desorption from sites associated with the Pt_n clusters.

The temperature dependence for desorption of intact C_2D_4 is different for the two cluster sizes. For Pt_4 , during the 1st TPD/R run, the desorption appears bimodal, with a strong and relatively sharp peak near 250 K, followed by a shoulder in the 350-400 K range, with a rapid intensity drop above 400 K. For Pt_7 , C_2D_4 desorption grows more slowly at low temperatures, peaking broadly around 300 K, and declining gradually above 400 K. According to the DFT calculations, the ethylene binding energy of the $\text{C}_2\text{H}_4/\text{Pt}_4/\text{SiO}_2$ global minimum structure, where the ethylene is bound in the di- σ mode, is roughly 0.14 eV stronger than in the second local minimum structure (23% population at 700 K), where ethylene is π -bonded. More detailed discussion can be found in the DFT analysis section.

For the 1st run on both Pt₄ and Pt₇, significant D₂ desorption starts just below 300 K and peaks broadly around 440 K, declining to baseline above 600 K. The D₂ signal is significantly larger for Pt₇ than Pt₄. In one experiment, the heat ramp was extended to 1000 K to check for additional C₂D₄ or D₂ desorption above 700 K. None was observed, suggesting that dehydrogenation and desorption go to completion by 700 K. The behavior observed here for Pt₄/SiO₂ and Pt₇/SiO₂ is similar to that observed for Pt_n/Al₂O₃ (n =4, 7), with intact C₂D₄ desorption peaking near 300 K, and D₂ desorption in the ~300 – 600 K range.¹

The integrated numbers of C₂D₄ and D₂ molecules desorbing from each sample are listed in **Table 1**, and because we know the Pt coverage precisely (1.5×10^{14} atoms/cm²), the integrated desorption numbers are given as molecules *per* Pt atom. To correct the numbers for the contribution of desorption from the SiO₂ substrate, ~0.02 C₂D₄ molecules/Pt atom should be subtracted. With this correction, we find that ~1.4 and ~2.1 intact C₂D₄ molecules desorb *per* Pt₄ and Pt₇ cluster, respectively, with the corresponding D₂ desorption being ~0.33 and ~0.77 D₂ molecules *per* cluster. Given that D₂ desorption goes to completion before termination of the heat ramp, the total number of C₂D₄ adsorbed *per* cluster can be estimated as #C₂D₄ desorbing + 0.5 #D₂ desorbing, giving ~1.6 and ~2.5 C₂D₄ adsorbed *per* Pt₄ and Pt₇, respectively. In theoretical modeling of Pt₄/SiO₂, we therefore considered coverages of one and two ethylene molecules *per* cluster. As expected, the number of adsorbed ethylene *per* cluster increases with cluster size, however, on a *per* Pt atom basis, slightly more ethylene adsorbs on Pt₄. This effect is consistent with the observation by ISS,² that Pt₇/SiO₂ has a smaller fraction of its Pt atoms in the surface layer, and thus presents fewer ethylene binding sites.

Table 1. Numbers of C₂D₄ and D₂ molecules desorbing *per* Pt atom from Fig. 1.

TPD Run:	Pt ₄ /SiO ₂		Pt ₇ /SiO ₂	
1st	0.350 C ₂ D ₄ /Pt	0.083 D ₂ /Pt	0.303 C ₂ D ₄ /Pt	0.110 D ₂ /Pt
2nd	0.340 C ₂ D ₄ /Pt	0.076 D ₂ /Pt	0.282 C ₂ D ₄ /Pt	0.066 D ₂ /Pt
3rd	0.270 C ₂ D ₄ /Pt	0.046 D ₂ /Pt	0.226 C ₂ D ₄ /Pt	0.050 D ₂ /Pt
4th	0.270 C ₂ D ₄ /Pt	0.024 D ₂ /Pt	0.187 C ₂ D ₄ /Pt	0.028 D ₂ /Pt

Fig. 1 also shows the 4th TPD/R run for each sample. Two significant changes are observed: the amount of ethylene desorbing is lower than in the 1st run, and the desorption occurs at lower temperatures. In addition, D₂ desorption is substantially weaker, compared to the 1st TPD/R run. The changes are qualitatively similar for the two cluster sizes, but more dramatic for Pt₇, where more dehydrogenation occurred in the 1st run. These changes imply that substantially less ethylene adsorbs at 180 K, and that the decrease primarily affects the more stable binding sites responsible for desorption at higher temperatures. As will be shown shortly, stronger binding typically corresponds to the di-σ mode of ethylene attachment, which is a precursor for dehydrogenation, which then poisons those sites by carbon deposits. As shown in **Fig. S1**, the 2nd, 3rd, and 4th TPD/R runs are quite similar, implying that most of the changes to the binding site distribution occur in the 1st TPD/R run. In the 4th TPD run, the differences between Pt₄/SiO₂ and Pt₇/SiO₂ are weaker than in the first, but the Pt₄ sample still had significantly more ethylene desorbing, and with sharper temperature dependence, compared to the Pt₇ sample. Given that both samples had the same total number of Pt atoms, the samples clearly retained at least some memory of the deposited cluster size after repeated TPD/R runs.

Run-to-run losses in the number of C₂D₄-Pt sites selectively affects the most-strongly bound C₂D₄-Pt sites, and because these are most likely to catalyze dehydrogenation, a run-to-run reduction in D₂ desorption is expected, and observed. Given the observation of D₂ desorption, the loss of C₂D₄ binding sites in repeated C₂D₄ TPD runs is at least partially attributable to poisoning by carbon deposition. We show below using XPS that repeated ethylene TPD runs lead to carbon deposition, although the precise amount was difficult to measure because the sensitivity for carbon is relatively low, and the Pt coverage (where C is depositing) is also very low.¹ DFT calculations on Pt₈/Al₂O₃ and Pt₈/Al₂O₃ with a carbon atom deposited were done to examine changes in cluster morphology and energetics, showing that deposition of electrophilic C causes some rearrangement in cluster geometry.¹ Note, however, that supported Pt_n clusters are expected to be quite dynamic under reaction conditions, sintering is also likely.

Because we have $\sim 3 \times 10^{-11}$ Torr of CO background in our UHV system, we always monitor CO desorption during TPD/R experiments. Here, ~ 0.2 CO molecules desorbed *per* Pt atom during the 1st run, with substantially less in subsequent runs. This CO contamination level is ~ 20 times larger than would be expected if CO sticks only when impinging directly on a Pt site, and shows that for small, well dispersed clusters, substrate-mediated adsorption (reverse spillover) substantially amplifies the contamination rate. Assuming that CO competes with C₂D₄ for binding sites, there probably would have been additional C₂D₄ and D₂ desorption observed in the 1st TPD/R runs in absences of CO, and the difference between the 1st and subsequent runs would have been larger.

Analogous C_2D_4 TPD/R experiments for PtSn alloy clusters are shown in **Fig. 2**, with all four TPDs shown in **Fig. S2**. In this case, the 1st run was done just after completing the $H_2/SnCl_4/H_2$ exposure process used to deposit Sn, and prior to any heating. At this point there would have been H as well as a small amount of Cl adsorbed on the clusters.² Therefore, it is not surprising that the amount of C_2D_4 desorbing in this 1st run is substantially smaller than in the 1st run for Pt_n/SiO_2 , because many C_2D_4 binding sites would have been blocked during the 180 K C_2D_4 exposure. During this 1st TPD/R run, significant HCl desorption was observed (**Fig. S3.**), and no Cl was

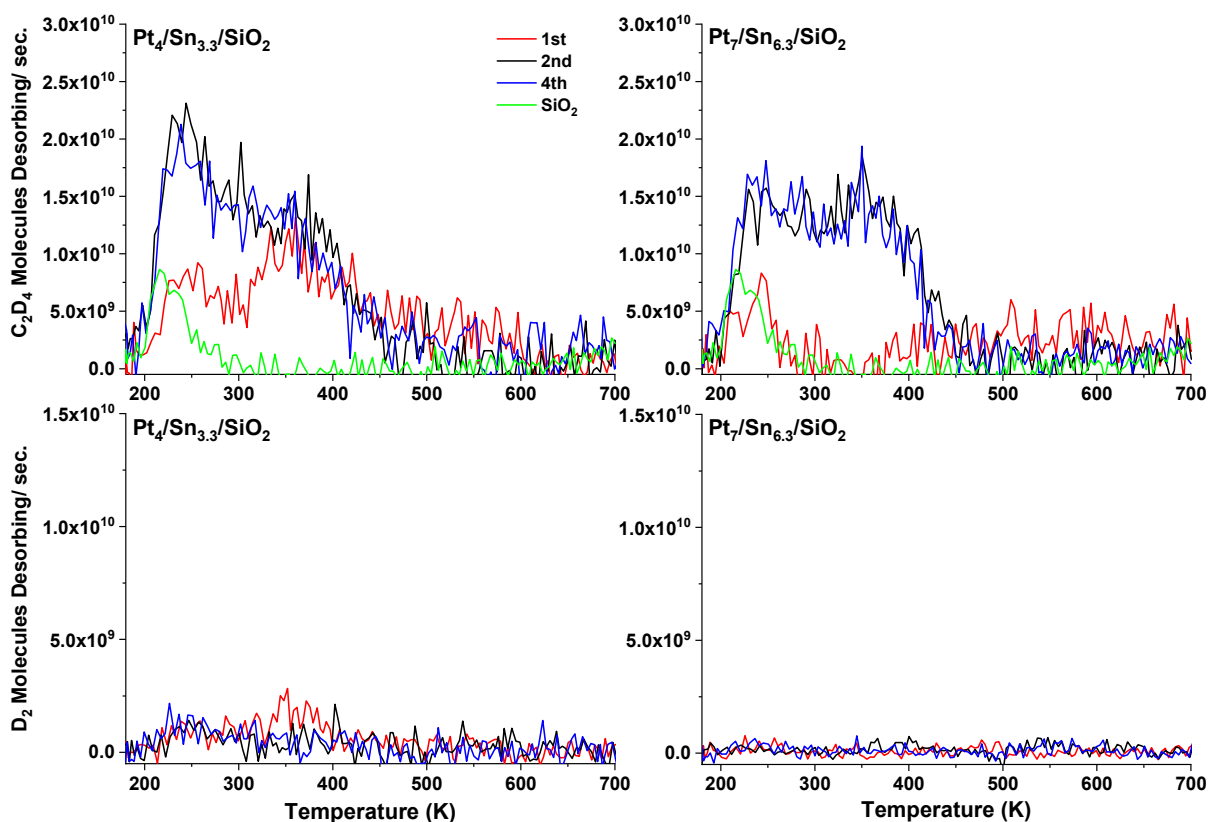


Figure 2. Desorption of C_2D_4 (top) and D_2 (bottom) from the first (red), second (black), and fourth (blue) C_2D_4 TPD/R run. Each spectra was collected after a 10 L dose of C_2D_4 to Pt_n/SiO_2 ($n = 4, 7$) at 180 K. C_2D_4 desorption from bare SiO_2 treated with 1 ALD cycle is also plotted (green) – no D_2 was observed in that experiment.

detectable by TPD/R, ISS, or XPS after the 1st run. H₂ desorption was not monitored due to large mass 2 background, but 700 K is well above the temperature where hydrogen desorbs from Pt_n.¹

In the 2nd TPD/R run on each sample, the amount of C₂D₄ desorbing increased substantially, indicating that desorption of HCl and H₂ during the 1st run left more binding sites accessible to C₂D₄. Therefore, we feel that the correct comparison is of the 2nd TPD/R run for Pt_nSn_x/SiO₂, with the 1st run for the Pt_n/SiO₂ samples. As before, the number of the C₂D₄ molecules desorbing *per* Pt atom in the 2nd, 3rd, and 4th TPD/R runs is given in **Table 2**.

Table 2. Numbers of C₂D₄ molecules desorbing per Pt atom from Fig. 2 and Fig. S2.

TPD Run:	Pt ₄ Sn _{3.3} /SiO ₂	Pt ₇ Sn _{6.3} /SiO ₂
2nd	0.190 C ₂ D ₄ /Pt	0.176 C ₂ D ₄ /Pt
3rd	0.210 C ₂ D ₄ /Pt	0.170 C ₂ D ₄ /Pt
4th	0.190 C ₂ D ₄ /Pt	0.174 C ₂ D ₄ /Pt

There are several important points of comparison with the results for pure Pt_n/SiO₂. First, there was no significant D₂ desorption in any run on the Pt_nSn_x/SiO₂ samples, i.e., all ethylene desorbed intact. The absence of D₂ desorption implies that there should be little if any carbon deposition. **Fig. S4** summarizes an XPS experiment that shows substantial carbon deposition in repeated TPD/R runs on Pt_n/SiO₂, and the complete absence of carbon deposition for Pt_nSn_x/SiO₂ under identical conditions.

Also consistent with the absence of carbon deposition, is the observation that once the H and Cl were desorbed during the 1st run, there was little change in the intensity or temperature dependence of C₂D₄ desorption in TPD runs two through four, compared to the substantial loss of intensity and shifts to lower temperatures observed for pure Pt_n/SiO₂. Additionally, the number of C₂D₄ molecules adsorbing during the 180 K dose was ~50% smaller for the Pt_nSn_x, compared to the pure

Pt_n, presumably due to site blocking by Sn atoms (note difference in vertical scales). Finally, for the Pt_nSn_x/SiO₂ samples there are cluster size effects on the desorption temperature dependence, weaker than the size effects observed for Pt_n/SiO₂, but which are quite persistent in repeated runs. From the perspective of improving the stability of sub-nano Pt cluster catalysts under high temperature hydrocarbon rich conditions, the absence of dehydrogenation (i.e., of carbon deposition) and the stability of the samples in repeated TPD/R runs are both important.

The C₂D₄ thermal desorption spectra were fit to extract desorption energy distributions, $\theta(E_{\text{des}})$, as described in the supporting information. An example fit is shown in **Fig. S5**, and the $\theta(E_{\text{des}})$ distributions for the 1st C₂D₄ TPD on Pt₄/SiO₂ and the 2nd C₂D₄ TPD on Pt₄Sn_{3.3}/SiO₂ are compared in **Fig. 3**. $\theta(E_{\text{des}})$ distributions for Pt₇/SiO₂ and Pt₇Sn_{6.3}/SiO₂ are shown in **Fig. S6**. Three features were included in the $\theta(E_{\text{des}})$ distributions to fit the experimental temperature dependences: a small feature with $E_{\text{des}} < 0.6$ eV attributed to desorption from SiO₂ sites, a larger feature with $0.6 < E_{\text{des}} < 1.2$ eV attributed to desorption from cluster sites, and a second feature with $0.8 < E_{\text{des}} < 1.6$ eV also attributed to desorption from cluster sites. Note that there is little difference in the range of E_{des} observed for Pt_n and Pt_nSn_x, consistent with the modest differences in desorption temperatures.

The effects of Sn-alloying on the Pt_n/SiO_2 system should be compared to the effects of Sn alloying on ordered PtSn surface alloys studied by Koel and co-workers.³¹⁻³² In both cases, ethylene dehydrogenation, leading to carbon deposition, is strongly suppressed, compared to pure Pt_n/SiO_2 or to Pt(111), but the mechanism appears to be different. For the PtSn surface alloys, the saturation ethylene coverage was Sn-independent, whereas for the clusters, Sn significantly reduced the coverage. For the surface alloys, the ethylene desorption temperature dropped with increasing Sn coverage from

~ 285 K for pure Pt(111)³⁶ to 184

K for the $\sqrt{3} \times \sqrt{3} R30^\circ$ alloy

which has 1:2 Sn:Pt ratio in the

surface layer. Hook *et al.* used

DFT to examine ethane

dehydrogenation over PtSn

surface alloys, finding,

consistent with the experiments

of Koel and co-workers, that Sn

depresses the alkene desorption

energy below the barrier for

dehydrogenation, due to a

combination of geometric and

electronic effects.³³ Thus in the

surface alloys, the suppression

of carbon deposition appears to

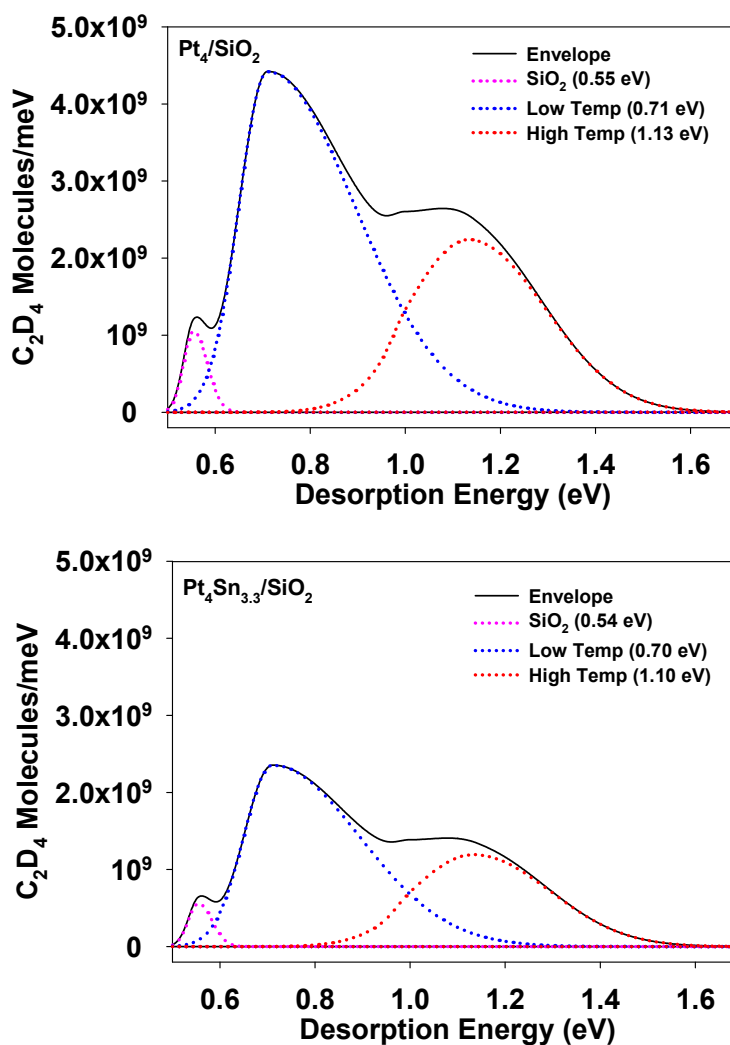


Figure 3. Energy desorption (E_{des}) profiles for Pt_4/SiO_2 (top) and $\text{Pt}_4\text{Sn}_{3.3}/\text{SiO}_2$ (bottom).

be largely due to the reduction in ethylene binding energy. This was also the conclusion in our study of the effects of boron addition to $\text{Pt}_n/\text{alumina}$ model catalysts,⁴ where boration shifted the ethylene desorption temperatures into the cryogenic range, thereby suppressing dehydrogenation. In contrast, for the Pt_n vs. Pt_nSn_x clusters here, there is no significant difference between the ethylene desorption temperatures or the extracted E_{des} distributions, suggesting that suppression of dehydrogenation/carbon deposition must result from a different mechanism.

ISS probing of the effects of TPD/R.

ISS experiments were carried out to probe differences in the structure of the Pt_n and Pt_nSn_x samples, and to provide insight regarding the changes in C_2D_4 and D_2 desorption behavior that occur in multiple TPD runs for Pt_n/SiO_2 . Peaks in ISS data result mostly from events in which He^+ scatters from a single atom in the surface layer, such that the retained energy, E_k/E_{k0} , depends on the target atom mass.³⁷ Multiple scattering, and scattering from atoms deeper in the surface result in low ion survival probability (ISP), and contribute mostly to the featureless background at low

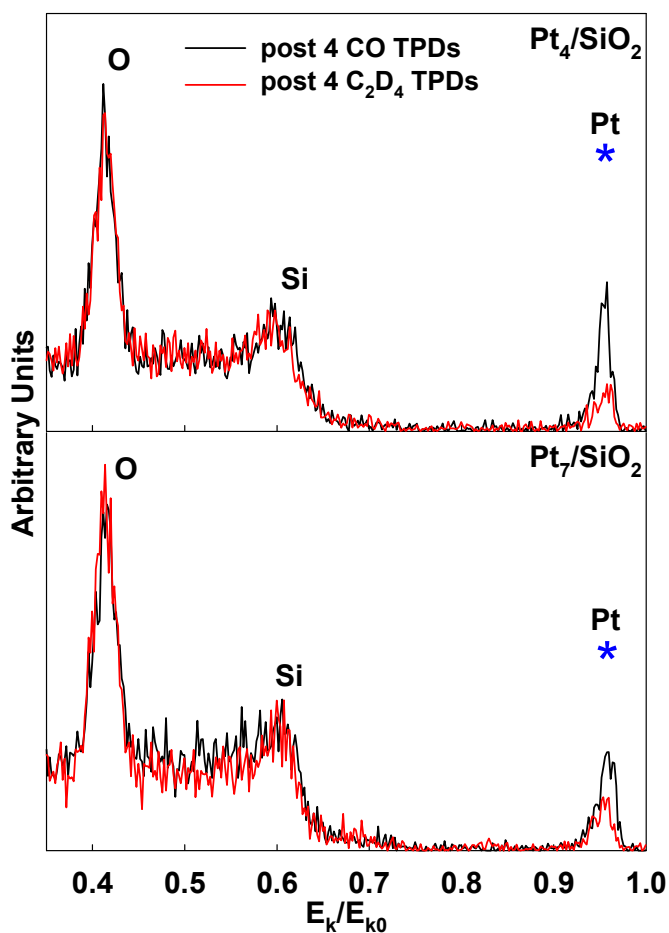


Figure 4. Raw ISS spectra for Pt_n/SiO_2 samples after they have undergone four CO TPDs to 700 K (black) and four C_2D_4 TPDs (red).

E_k/E_{k0} . The usefulness of ISS here is that it is sensitive both to the cluster morphology and to the presence of adsorbates on the cluster surface, due to shadowing, blocking, and ISP effects.³⁸⁻⁴⁰

Fig. 4 summarizes ISS data for Pt₄ and Pt₇ samples after four cycles of C₂D₄ TPD/R. The results are compared to ISS (on separate samples) after four cycles of CO TPD under identical conditions, to show the effects of TPD with a non-coking adsorbate. Peaks for O, Si, and Pt are observed. For comparison, the intensities of the Pt peak for as-deposited, unheated Pt_n/SiO₂ samples are indicated in **Fig. 4** by blue stars. The O and Si intensities for the as-deposited samples are not shown because they are essentially identical to the post-TPD/R results in the figure. All the samples were prepared with the same total number of Pt atoms, therefore, if the same fraction of Pt atoms are exposed in the surface layer, the Pt ISS intensities should be identical. It can be seen that the as-deposited Pt intensity is highest for Pt₄, and ~28% lower for Pt₇, indicating that some of the Pt atoms in Pt₇/SiO₂ are not in the surface layer, as would be the case for a 3D cluster structure.

After four CO TPD runs, the Pt intensities for both sizes decrease significantly. This decrease suggests significant sintering of the clusters, although there may also be some contribution from isomerization to structures with fewer atoms in the surface layer.^{1-2, 39, 41-42} To test for the possibility that CO adsorption might affect the sintering/isomerization process, a separate experiment was performed in which a Pt₄/SiO₂ sample was simply flashed to 700 K four times in the absence of any deliberate adsorbate exposure. The resulting Pt ISS intensities were identical to those observed for clusters having undergone four CO TPDs, i.e., the effects are thermal, with no significant effect of small CO exposures.

The decreases in Pt ISS signal after 4 C₂D₄ TPD/R experiments are substantially larger. This could be taken as evidence that C₂D₄ enhances sintering, however, we know from the observation of D₂ desorption and the appearance of carbon in post-TPD/R XPS, that there is carbon deposition on these samples. The ISS results are, therefore, confirmation that this carbon is deposited on, and blocks access to Pt sites, as opposed to depositing on the SiO₂ support. Given that the clusters may also be sintering during TPD/R, it is most useful to compare the carbon deposition on a *per* Pt atom, rather than a *per* cluster basis. From the 1st TPD/R run data in (Fig. 1), we can see that Pt₄ has a higher density of C₂D₄ binding sites (0.43/Pt atom), than Pt₇ (0.36/Pt atom), and a lower D₂/C₂D₄ desorption ratio (0.23), compared to 0.36 for Pt₇. If we assume each D₂ desorption results in deposition on one C atom, then for Pt₄ the 1st TPD/R run deposits ~0.1 C/Pt atom, while for Pt₇, it should deposit slightly more – 0.13 C/Pt. As can be seen from Fig. S1 the differences are smaller in subsequent TPD/R runs. After four runs, the final Pt ISS intensities are similar for the two clusters.

Analogous ISS experiments for Pt_nSn_x/SiO₂ are shown in Fig. 5. Sets of

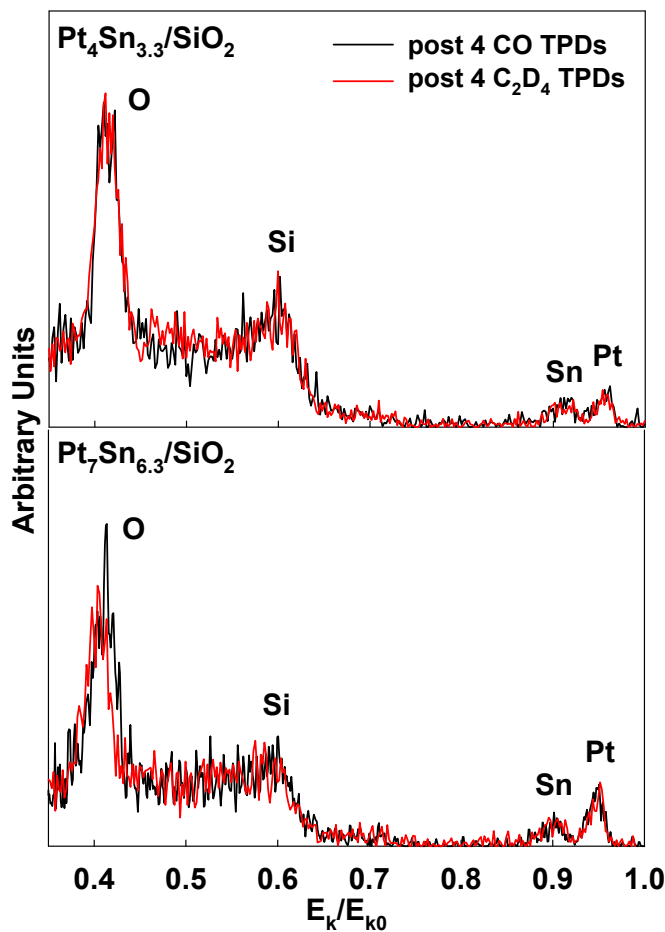


Figure 5. Raw ISS Scans for Pt₄Sn_{3.3}/SiO₂ and Pt₇Sn_{6.3}/SiO₂ after four C₂D₄ TPDs (red) and 4 CO TPDs (black)

$\text{Pt}_n\text{Sn}_x/\text{SiO}_2$ samples were prepared and exposed to either four C_2D_4 TPD/R runs, or four CO TPD runs, then examined by ISS. It can be seen that the O and Si peaks are similar to those in the Pt_n/SiO_2 samples, as expected because Sn deposits primarily on the Pt clusters,² but that the Pt peak is substantially less intense, and a peak for Sn is observed.

It is also interesting to compare the post TPD ISS to ISS measured just after the $\text{H}_2/\text{SnCl}_2/\text{H}_2$ treatment (prior to any heating), and after the initial heating to drive off H

and Cl. For the treated, unheated sample, the Sn peak is larger and the Pt peak is smaller (Sn:Pt ratio ≈ 2) compared to those in **Fig. 5**, as might be expected for Sn initially deposited on top of the Pt clusters. After initial heating to drive off H and Cl, the spectrum is essentially identical to the post-TPD spectra shown in **Fig. 5**. i.e., neither of the repeated TPD/R experiments has any

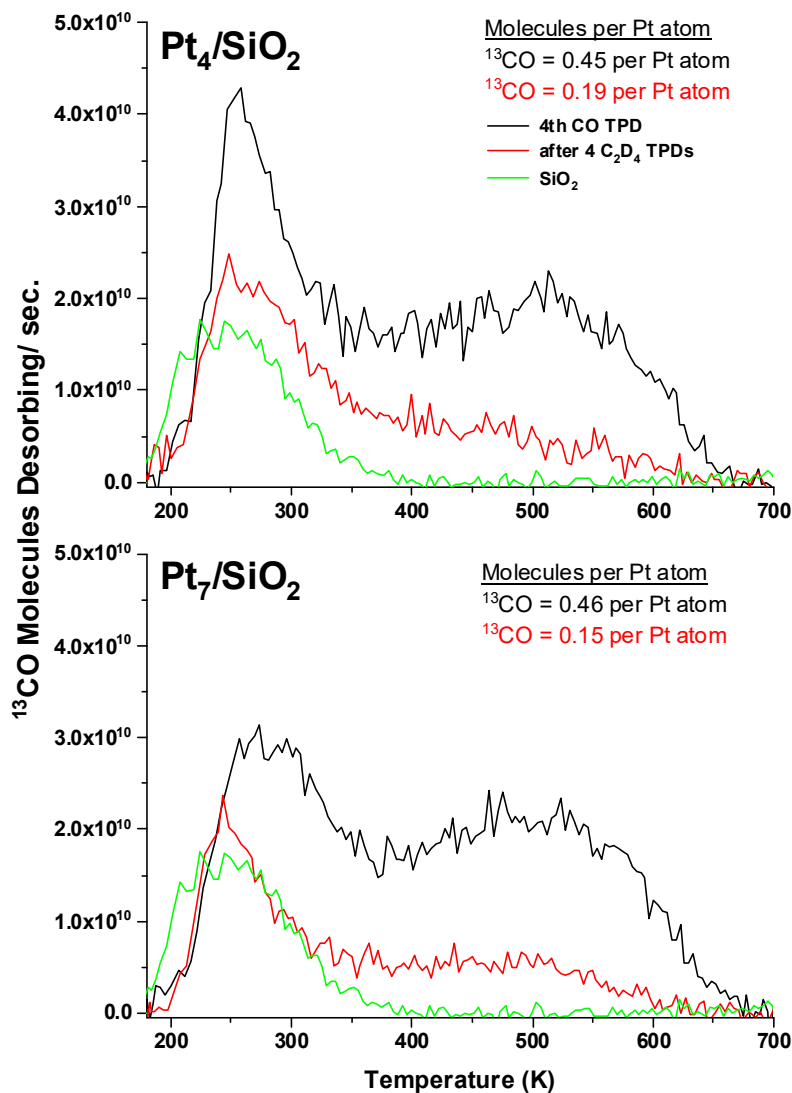


Figure 6. ^{13}CO TPD after four CO TPDs (black line) and a ^{13}CO TPD after four C_2D_4 TPDs for Pt_n/SiO_2 (red). CO desorption from SiO_2 is also shown (green)

significant effect on the ISS. The stability with respect to repeated C₂D₄ TPD/R runs is a consequence of the absence of carbon deposition on the clusters. Consistent with the TPD/R data in **Fig. 2**, ISS shows that Sn alloying significantly reduces the number accessible Pt binding sites, but that the sites present are quite stable.

CO desorption as a probe of accessible Pt sites.

The final approach used to probe the effects of repeated heating and C₂D₄ exposure on the clusters was to carry out ¹³CO TPD after the C₂D₄ TPD/R sequence (on different samples than those used for ISS characterization). **Fig. 6** compares CO TPD measured for a sample first subjected to four C₂D₄ TPD/R runs (red) to the CO desorption measured in the 4th in a series of sequential CO TPDs (black). For comparison, CO desorption from the SiO₂

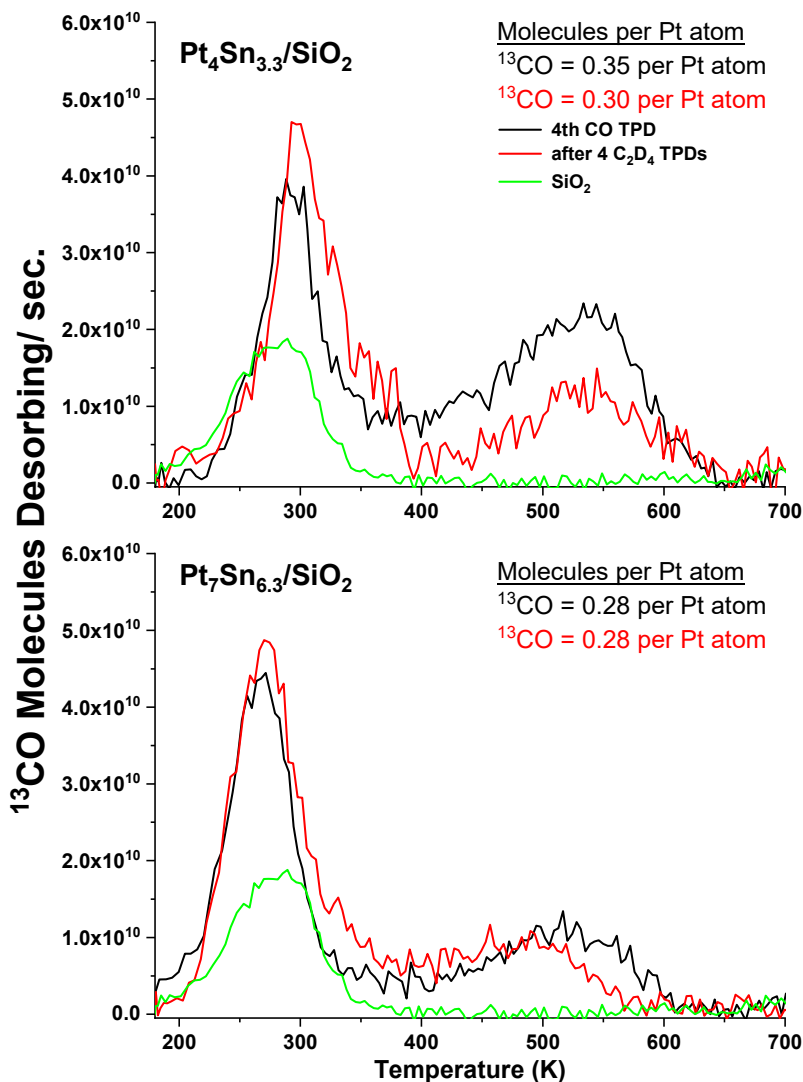


Figure 7. CO TPD spectra of Pt_nSn_x/SiO₂ after four CO TPDs (black) and four C₂D₄ TPDs (red). The 2nd ¹³CO TPD from H₂/SnCl₄/H₂ – SiO₂ is also shown (green).

substrate is also shown (green). The ion signals were converted to numbers of CO molecules using the process described above, and the integrated number of CO molecules indicated in the text on each frame of the figure have been corrected for CO desorbing from the SiO₂ substrate, i.e., the numbers correspond to the CO desorbing from Pt sites. For Pt₄ and Pt₇, repeated C₂D₄ TPD/R results in far larger attenuation of Pt-associated CO binding sites, and particularly of the sites with high E_{des} , compared to repeated CO TPD runs. This mirrors the ISS results, where C₂D₄ TPD/R caused a much larger Pt intensity attenuation.

Fig. 7 shows the analogous results for Sn ALD-treated samples. In this case, the desorption shown for the substrate (“H₂/SnCl₄/H₂ – SiO₂”) is for SiO₂ subjected to the Sn ALD treatment, then heated to drive off any residual Cl or H, before being probed by CO TPD. For the Sn-treated samples, the differences in CO desorption for samples after repeated CO TPDs vs. repeated C₂D₄ TPD/R runs are much smaller than for the Sn-free Pt_n/SiO₂ samples. For Pt₄Sn_{3.3}, repeated C₂D₄ TPD/R runs resulted in a shift in intensity from the higher to the lower temperature desorption feature, with a ~14% decrease in the integrated number of CO molecules desorbing, compared to the effects of four CO TPD runs. For Pt₇Sn_{6.3}, similar, but smaller changes in the desorption temperature dependence were observed, and the integrated number of CO molecules desorbing was identical for the samples subjected to multiple CO or C₂D₄ TPD experiments. It is not clear why the difference between the effects of C₂D₄ and CO TPD/R was larger for the smaller cluster size, however, for such a small cluster it would not be surprising if the degree of sintering occurring during the TPD heat ramps is affected by whether the clusters are saturated by CO or by C₂D₄. Note that in the analogous experiments on pure Pt₄, both the low and high temperature desorption features decreased significantly more after C₂D₄ TPD/R, such that the decrease in total number of

CO binding sites was almost 60% bigger than in multiple CO TPDs. Clearly, the carbon deposition occurring during C₂D₄ TPD on pure Pt_n has a large effect on the site availability.

DFT Analysis of the Effects of Sn Alloying on Ethylene Binding and Dehydrogenation.

Supported cluster catalysts can have many structural isomers accessible in the ≤ 700 K temperature regime of interest here.⁴³⁻⁴⁶ These isomers can have similar energies, despite having different morphologies, with different morphologies favoring different binding sites and chemical character. It is important to consider these different isomers in the mechanism, because they are expected to be thermally-populated due to high fluxionality of the clusters in this temperature regime.^{22,47} Due to the large amount of sampling needed for the reliable exploration of the potential energy surfaces, we focus the theory on Pt₄/SiO₂ and Pt₄Sn₃/SiO₂.

From the experiments, an average of ~ 1.4 C₂D₄ molecules are adsorbed *per* Pt₄ cluster; therefore, each isomer has also been optimized with either one or two C₂H₄ molecules adsorbed. Structures obtained from the global optimization are shown in **Figs. 8 and S7**. Note that C₂H₄ is able to bind in several configurations depending on the isomer. For instance, C₂H₄ in the global minimum structure of C₂H₄/Pt₄/SiO₂ preferentially binds in the di- σ binding mode, whereas in the global minimum of (C₂H₄)₂/Pt₄/SiO₂ there is one di- σ bound ethylene, and one π -bound ethylene. Note that other higher energy isomers, which are thermally accessible at higher temperatures, can have different C₂H₄ binding preferences than the global minimum, as shown in **Fig. 8**. Previously, it was shown that the stronger di- σ interaction favors dehydrogenation.¹

Referencing the literature augments our interpretations, as ethylene dehydrogenation has been thoroughly studied via DFT and various surface analysis methods over extended Pt surfaces. For example, for temperatures around 100 K, LEED showed ethylene adsorption having a clear preference for di- σ adsorption to Pt(100)⁴⁸ and Pt(111).⁴⁹ In contrast, EELS analysis of stepped/lower-coordinated Pt sites (Pt(210) and Pt(110)) showed π -binding of ethylene.⁵⁰ The di- σ binding was probed using TPD of mixed C₂D₄ and C₂H₄ adsorbed on Pt(111) by Janssens *et al.*, who reported recombinative desorption of isotope-scrambled ethylene at ~285 K, indicating dissociative adsorption.⁵¹ Just above the 285 K desorption peak, hydrogen evolution begins, with the first H loss resulting in a surface-bound ethylidyne, although this is largely considered to be a

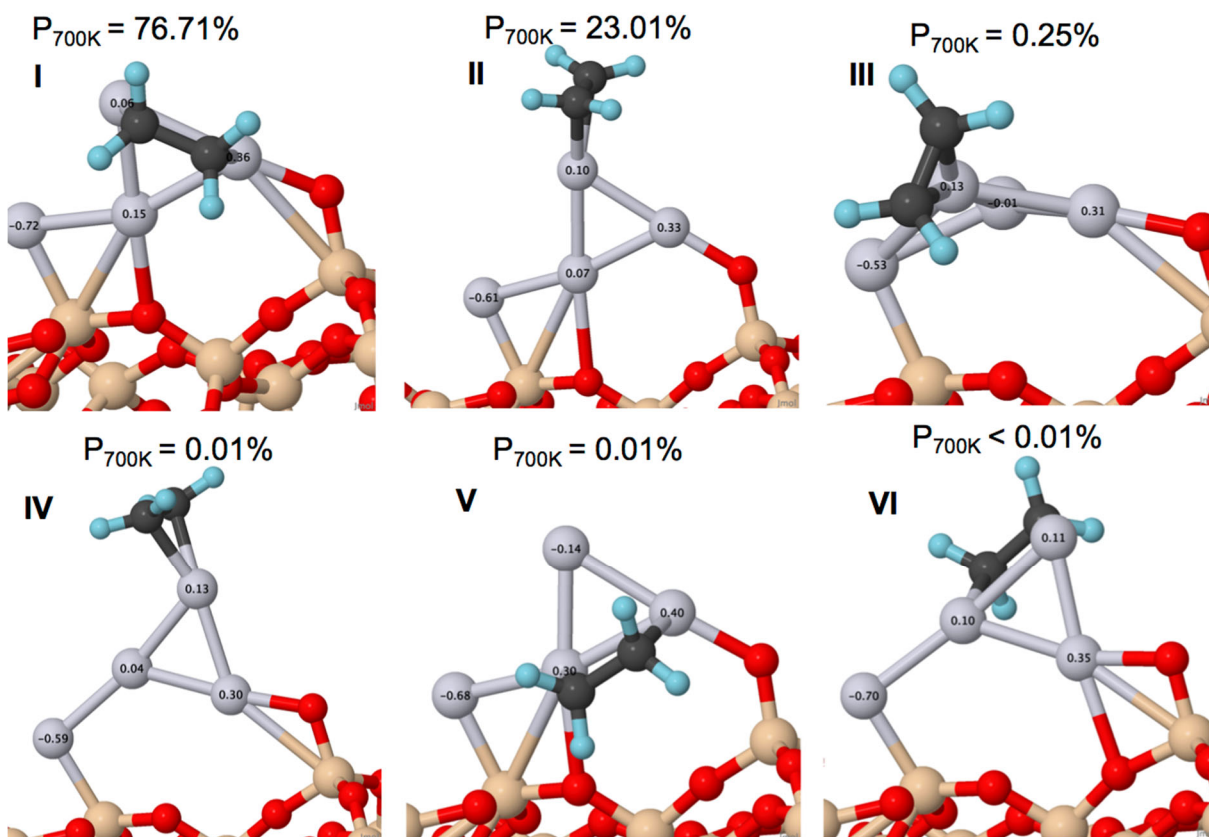


Figure 8. Thermally-accessible geometries of C₂H₄/Pt₄/SiO₂ obtained from global optimization calculations. The geometries of (C₂H₄)₂/Pt₄/SiO₂ are shown in **Fig. S7**.

spectator between the first and remaining H dissociation events.⁵²⁻⁵⁴ As the sample temperature continues to increase, additional dehydrogenation occurs, indicated by additional H₂ desorption until 700 K. Results for the π -bound molecules on low-coordinated stepped surfaces were quite different. For example Yagasaki *et al.* studied C₂H₄ decomposition on Pt(210) and reported that some desorbs intact around 250 K, but the residual π -adsorbed C₂H₄ undergoes dehydrogenation around 300 K, as shown by desorption of H₂ and detection of surface ethylidyne with both C atoms coordinated to the surface. Further heating the Pt(210) surface to 700 K drives dehydrogenation to completion.

Pt(110) showed different behavior, as reported by Yagasaki *et al.* Here, some of the π -adsorbed ethylene is isomerized to the di- σ mode by 160 K. From 270 K–330 K, it undergoes decomposition to both C atoms and ethylidyne surface species, while evolving methane and hydrogen. The strongly bound ethylidyne then completes dehydrogenation by 450 K. For comparison, an IR absorption study⁵⁵ was done on Al₂O₃-supported Pt nanoparticles around 180 K that resulted in three ethylene adsorption modes: π -adsorption, di- σ adsorption, and spontaneous ethylidyne formation. Interestingly, all π -adsorbed ethylene was found to desorb intact by room temperature, while the di- σ bound ethylene is converted to ethylidyne and hydrogen.

Interpretation of our DFT and experimental results in light of these results allows conclusions to be made about the mechanism in our Pt_n/SiO₂ experiments. The three structures I, II, and III shown in **Fig. 8** and structure I in **Fig. S7** each have significant contributions to the cluster ensemble and we thus expect surface-bound ethylene species to adsorb in both the π and di- σ modes. We consider the comment by Mohsin *et al.*, that ethylidyne can spontaneously form at this temperature (as a result of dissociation of surface ethylene). In a D₂ thermal desorption study for Pt(100), Pasteur *et al.* showed recombinative desorption between 250 K and 500 K.⁵⁶ Spontaneous D₂

desorption is therefore not expected; rather we would expect these species to exist as surface-bound.

The calculated structures for ethylene on bare Pt₄/SiO₂ offer some explanation for the ISS experiments, which were conducted at 150 K, where only the lowest energy isomers are accessible, and all Pt atoms are in the surface layer. This results in the highest scattering intensity for as-deposited Pt₄ clusters, when compared to larger, multilayered clusters.¹ At higher temperatures, the catalytic activity observed experimentally is a result of a linear combination of the populated structures and the mechanisms they individually promote. With a combination of binding modes, diverse chemical behavior is expected, where both intact desorption of ethylene and dehydrogenation of ethylene would be expected, as observed.

In bulk, calorimetric experiments by Anres *et al.* showed that PtSn has a highly negative enthalpy of formation.⁵⁷ Similarly, Liu and Ascencio reported DFT simulations for clusters of a few hundred atoms that found PtSn clusters to be energetically favorable compared to pure Pt clusters.⁵⁸ For sub-nano clusters, DFT shows that Sn incorporation to size-selected Pt clusters results in substantial electron transfer from Sn to Pt atoms, and reduces the fluxionality of the clusters, such that one isomer dominates the ensemble.² The dominant isomer is an intermixed Pt₄Sn₃ structure, with each atom showing a relatively high degree of coordination. From the chemistry perspective, one important result was that adding Sn quenches all unpaired spins on Pt, while in the pure Pt₄/SiO₂ system there are low energy isomers with unpaired electrons available for adsorbate binding.

To examine the effects of ethylene adsorption on PtSn clusters, DFT calculations were performed for ethylene adsorbed on both the global minimum Pt₄Sn₃/SiO₂ structure, and on several of the lowest energy isomers. The lowest energy isomer changes when ethylene is adsorbed, thus

we expect the isomer ensemble to change as the clusters are heated with adsorbed ethylene. The most stable isomers for $\text{C}_2\text{H}_4/\text{Pt}_4\text{Sn}_3/\text{SiO}_2$ are shown in **Fig. 9**, along with Boltzmann population and Bader charge data. Structures with two adsorbed ethylene molecules are shown in **Fig. S8**. As shown in **Fig. 9**, the most stable isomers for a single ethylene have it π -bonded to Pt atoms in the cluster, however, as shown **Fig. S8**, one isomer was found for $(\text{C}_2\text{D}_4)_2/\text{Pt}_4\text{Sn}_3$ in which one of ethylene molecules is bound with one C atom bound to Sn, and one to an adjacent Pt atom. Note that for a single ethylene, di- σ binding has been completely eliminated by incorporation of Sn into

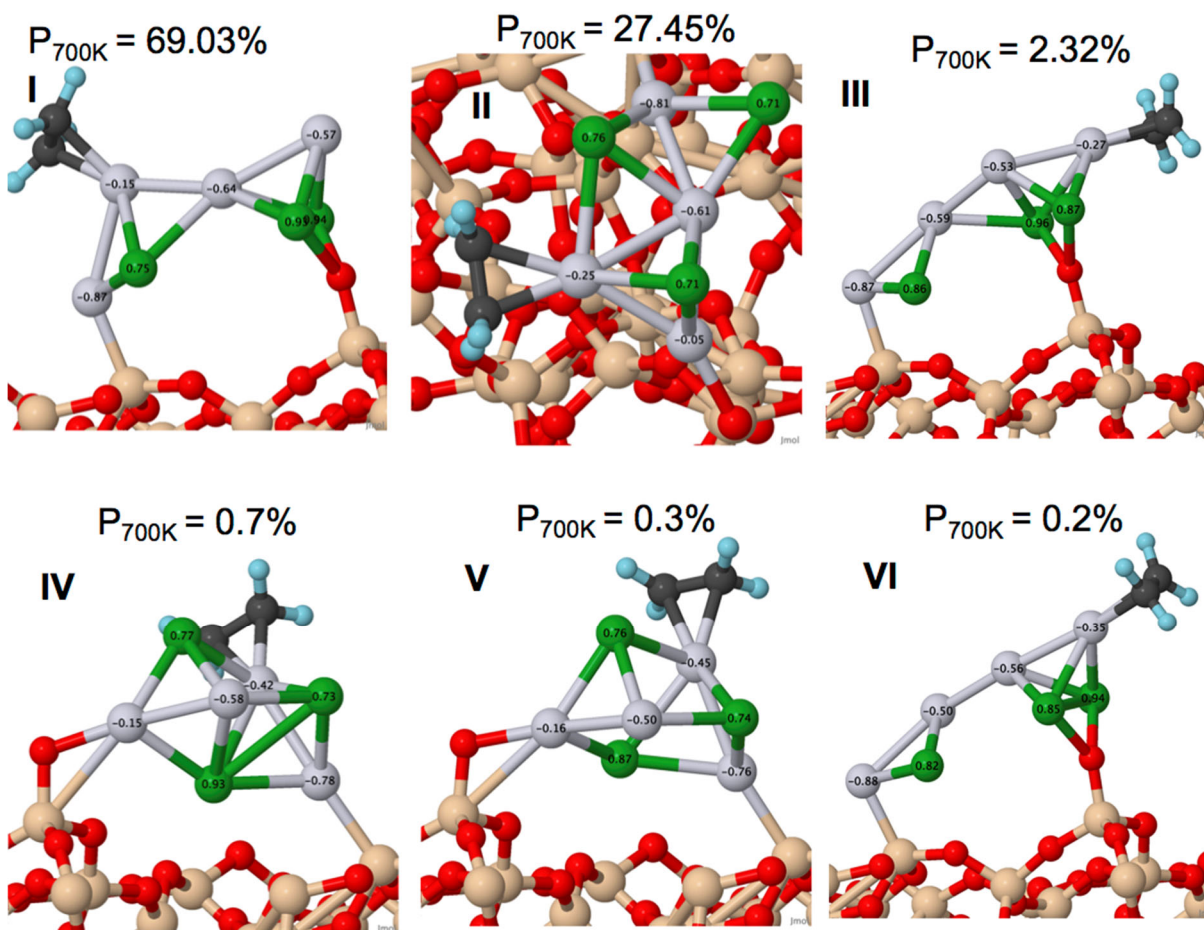


Figure 9. Thermally-accessible geometries of $\text{C}_2\text{H}_4/\text{Pt}_4\text{Sn}_3/\text{SiO}_2$ obtained from global optimization calculations. Note that the ensemble is dominated by C_2H_4 π -binding mode. The geometries of $(\text{C}_2\text{H}_4)_2/\text{Pt}_4\text{Sn}_3/\text{SiO}_2$ are shown in **Fig. S8**.

the Pt₄ clusters. Structure I is the preferred C₂H₄/Pt₄Sn₃/SiO₂ isomer, with greater than 69% of the population at 700 K. The only structure with di- σ C₂H₄ is structure II for adsorption of two ethylene molecules (**Fig. S8**). While there is still some diversity in the lowest energy isomer distribution, C₂H₄ is only able to adsorb via π interaction, which is expected to limit the catalytic branching toward the products of deeper dehydrogenation on the Pt₄Sn_{3.3}/SiO₂ catalyst.

In order to compare the barriers of C₂H₄ dehydrogenation on Pt₄/SiO₂ vs. Pt₄Sn₃/SiO₂, CI-NEB calculations were done on the three structures of Pt₄/SiO₂ and Pt₄Sn₃/SiO₂ that are most populated at 700 K. For every structure, the barrier to break each of the four C-H bonds is considered. The minimum energy pathway for each isomer along with the structures of reactants, transition states, and products are shown in **Fig. 10**. Additional CI-NEB reaction paths for other isomers and ethylene binding sites, along with the structures involved, are summarized in **Figs S9 - S13**.

The lowest reaction barrier of the most populated C₂H₄/Pt₄/SiO₂ structure is 0.95 eV, whereas this value for C₂H₄/Pt₄Sn₃/SiO₂ is 1.29 eV. Isomer II of C₂H₄/Pt₄Sn₃/SiO₂ has a more accessible low-energy path (1.00 eV) which makes it the most active of the three lowest-energy isomers of the system. This confirms our working hypothesis that the less stable isomers tend to be more reactive, and they must be considered in order to accurately describe the catalytic properties of dynamic catalysts. Of course, the contributions of the isomers II and III to the reaction is smaller because of their smaller presence in the ensemble (see **Figs. 8 and 9**).

Additionally, **Fig. 11** gives the values for the 700 K ensemble-average rate constants (k_{ens}) for C₂H₄/Pt₄/SiO₂ and C₂H₄/Pt₄Sn₃/SiO₂ along with the rate constant calculated for each isomer, and the contribution of that isomer to the ensemble. The results show that the Pt₄/SiO₂ ensemble is more active at 700 K toward ethylene dehydrogenation than the Pt₄Sn₃/SiO₂ ensemble. At lower temperatures, such as the ~300 K onset temperature for dehydrogenation, the difference would be

larger. These results confirm the experimental finding that introducing Sn to the cluster makes it

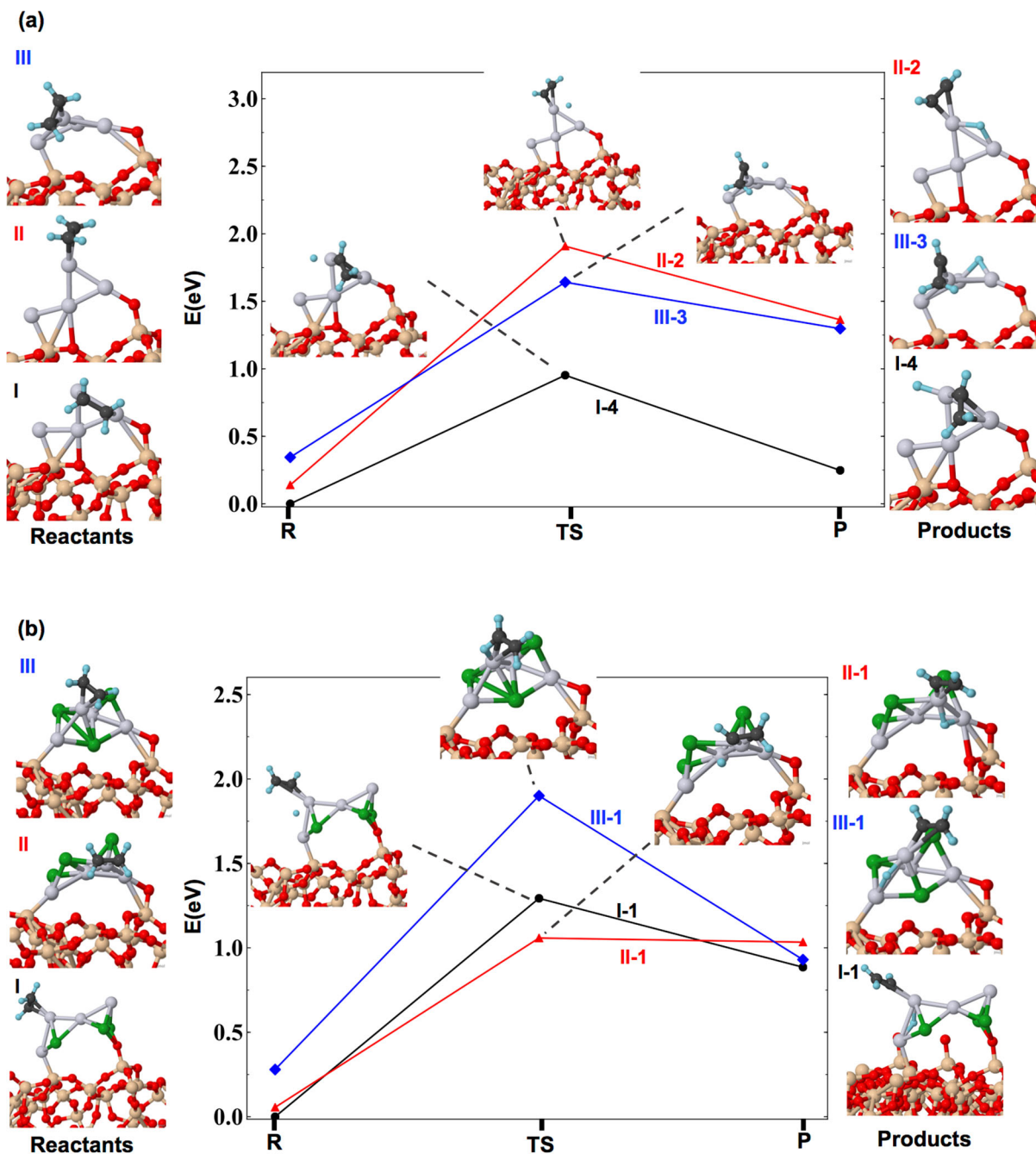


Figure 10. Lowest energy reaction profiles of breaking C-H bond obtained from CI-NEB calculations for each isomer of (a) $C_2H_4/Pt_4/SiO_2$ and (b) $C_2H_4/Pt_4Sn_3/SiO_2$ along with the structures of reactants, transition states, and products.

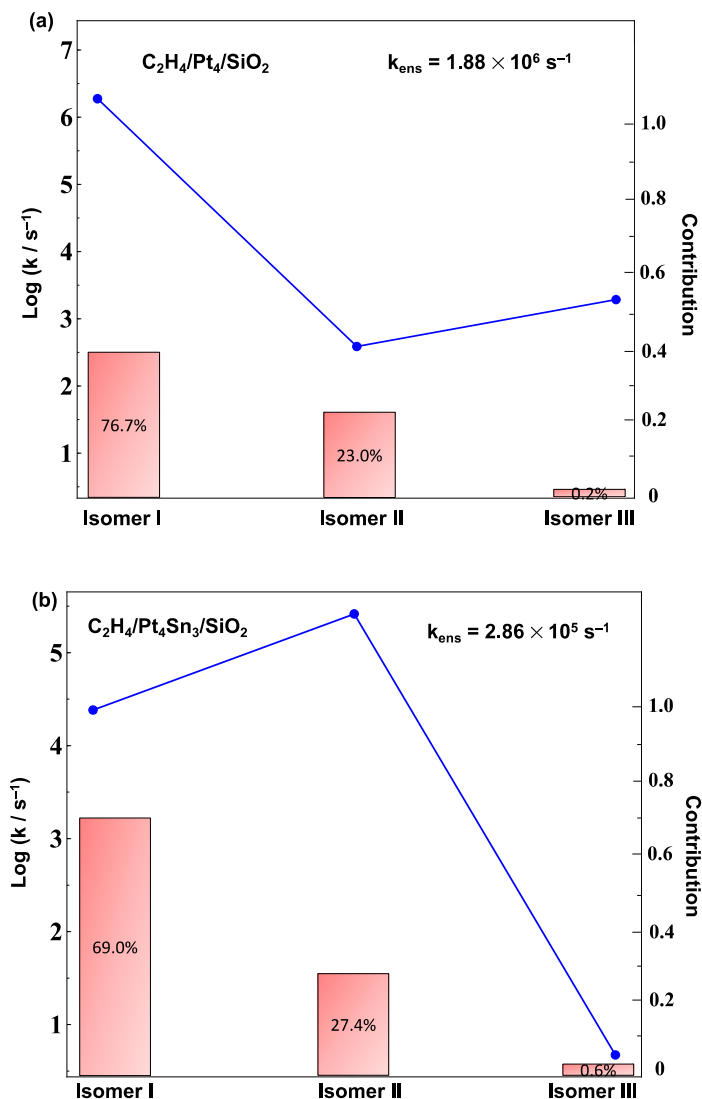


Figure 11. (a) Calculated rate constants along with their corresponding contribution to the k_{ens} at 700 K for each isomer of (a) $C_2H_4/Pt_4/SiO_2$ and (b) $C_2H_4/Pt_4Sn_3/SiO_2$. As expected, Pt_4/SiO_2 is more active than Pt_4Sn_3/SiO_2 toward ethylene dehydrogenation. harder for C_2H_4 to undergo dehydrogenation.

Another interesting result is that on many cluster isomers, two of the hydrogens of ethylene can be removed significantly more easily than the other two. For instance, according to the $C_2H_4/Pt_4/SiO_2$ isomer I reaction pathways in **Fig. S9**, the barriers corresponding to breaking C-H₃ and C-H₄, which are plotted as I-3 and I-4, are almost 2 eV lower than those of C-H₁ and C-H₂ (I-1

and I-2). This can be understood by structure analysis (**Fig. S10**): the Pt atoms on the top of the cluster are more undercoordinated and active than the Pt atoms attached to the surface; thus, placing the detached H atoms on the top Pt sites is favorable (on either atop or bridge sites).

Note that all reaction profiles obtained from CI-NEB calculations along with the structures can be found in **Figs. S9–13**, and the corresponding numerical data is summarized in **Table S1**. By comparing these structures, we find that on Pt₄Sn₃/SiO₂, in the product state, the Pt-C bonds between C₂H₃ and the catalyst are elongated, compared to those on Pt₄/SiO₂. This suggests that the product might more easily leave Pt₄Sn₃/SiO₂ (or recombine and leave), whereas it is more likely to undergo further dehydrogenation on Pt₄/SiO₂.

Additionally, the properties of the ensemble of clusters with one and two adsorbed C₂H₄ are summarized in **Tables S2 and S3**. As can be seen, the Pt₄ cluster has negative charge due to electron transfer from the support, while the charge of Pt₄Sn₃ is positive, as expected from the more electropositive nature of Sn. Moreover, the ethylene binding energy of Pt₄Sn₃/SiO₂ is ~0.7–0.8 eV weaker than that of Pt₄/SiO₂ as is clear from **Table S3**; this makes it easier for ethylene to desorb from the cluster rather than undergo further dehydrogenation.

Next, MD simulations were run for 10 ps at 700 K to allow sampling of the adsorbate and cluster motion. The average C-C bond distance in C₂H₄/Pt₄Sn₃/SiO₂ is 0.1 Å shorter than that in C₂H₄/Pt₄/SiO₂, consistent with its looser binding to the PtSn clusters, and indicating the bond being closer to double in character (**Figs. S14 and S15**). Furthermore, the average ∠PtCC bond angle in C₂H₄/Pt₄/SiO₂ is very close to the tetrahedral angle (104.94 °) showing the σ-bonding interaction between ethylene and the cluster. On the other hand, the average ∠HCC bond angle in C₂H₄/Pt₄Sn₃/SiO₂ is 120.47 ° showing a significant C-C double bond nature and π interaction between the adsorbate and the cluster. Note that during the MD simulations of C₂H₄/Pt₄Sn₃/SiO₂,

ethylene becomes partially detached from the cluster at 5.059 ps, which is shown in **Fig. S17**, whereas on $\text{C}_2\text{H}_4/\text{Pt}_4/\text{SiO}_2$ ethylene is always attached to the cluster. This again suggests that ethylene is more likely to desorb from the $\text{Pt}_4\text{Sn}_3/\text{SiO}_2$ surface, rather than remaining on the surface and undergoing dehydrogenation.

Ethane-to-ethylene conversion is the ultimate target for these catalysts, but in UHV experiments, it is infeasible to probe C_2D_6 dehydrogenation over Pt_n/SiO_2 and $\text{Pt}_n\text{Sn}_x/\text{SiO}_2$, because ethane does not stick at relevant temperatures. However, DFT can be useful to bridge the gap. We performed calculations of C_2H_6 dehydrogenation on the pure and Sn-alloyed Pt clusters, to show that PtSn clusters can actually dehydrogenate C_2H_6 and form the desired C_2H_4 product. **Fig. 12** shows the barriers corresponding to ethane dehydrogenation on the Pt_4/SiO_2 and $\text{Pt}_4\text{Sn}_3/\text{SiO}_2$ global minimum structures. The reaction barriers are 0.22 eV for Pt_4/SiO_2 , and 0.58 eV for $\text{Pt}_4\text{Sn}_3/\text{SiO}_2$, i.e. lower than the ones obtained for C_2H_4 dehydrogenation (0.96 eV and 1.30 eV, for Pt_4/SiO_2 and $\text{Pt}_4\text{Sn}_3/\text{SiO}_2$, respectively). The reason PtSn can dehydrogenate ethane relatively easily, but not ethylene, has to do with the type of sites required for the two reactions. Whereas di- σ ethylene activation requires the binding to two Pt atoms, ethane binds to a single Pt atom with both the H and the C atoms of the activated C-H bond. Such sites are available on both pure and Sn-alloyed Pt clusters. These results suggest that both catalysts should successfully dehydrogenate alkanes, whereas dehydrogenation of alkenes is harder, and further hindered by alloying of the cluster catalyst with Sn. This justifies the use of C_2H_4 as a model for selectivity of dehydrogenation catalysis.

In the past, we proposed that Si and Ge as new highly competitive alloying elements for Pt.⁵⁹⁻⁶⁰ Both Si and Ge have very similar effect on Pt clusters to the effect of Sn: mixing, Pt site separations, and electronic spin quenching. Both Ge and Si were shown to suppress

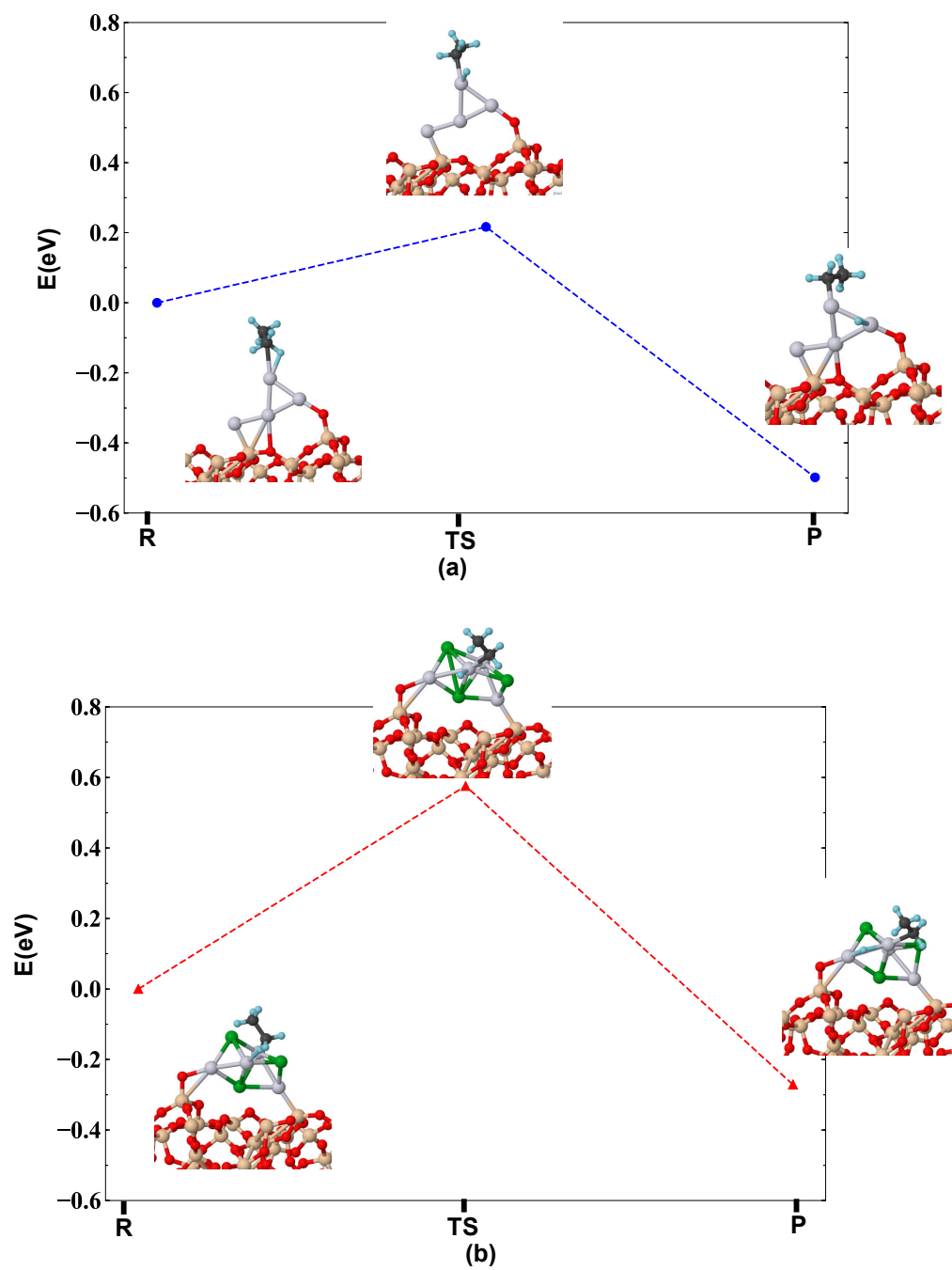


Figure 12. Lowest energy reaction profiles of breaking C-H bond obtained from CI-NEB calculations for the global minimum isomer of (a) $C_2H_6/Pt_4/SiO_2$ and (b) $C_2H_6/Pt_4Sn_3/SiO_2$ along with the structures of reactants, transition states, and products.

dehydrogenation beyond ethylene. However, for PtGe, the step of ethane dehydrogenation was actually accelerated compared to the process on pure Pt, and that is different from the effect of Sn, which makes ethane dehydrogenation less facile (though still quite accessible).

CONCLUSIONS

We have presented a study comparing the activity and selectivity of Pt_n/SiO_2 and $\text{Pt}_n\text{Sn}_x/\text{SiO}_2$ for ethylene desorption vs. dehydrogenation and carbon deposition. Alloying of sub-nano Pt_n clusters with Sn resulted in considerable improvement in selectivity by blocking the di- σ binding mode of ethylene, while preserving the π -mode. The origin of this selectivity is electronic and geometric. Adding Sn quenches all unpaired spins on Pt, which are required for the di- σ ethylene binding. Also, Sn intermixes with Pt and separates Pt atoms from each other, thus again preventing di- σ ethylene binding. This resulted in suppression of the dehydrogenation mechanism, allowing ethylene to desorb from the catalytic surface intact before decomposition into high binding energy coke precursor surface species. The improvement in catalyst selectivity thus results in an improvement in run-to-run stability, suggesting that sub-nano PtSn alloy clusters could be a promising candidate for high temperature dehydrogenation catalysts.

On the mechanistic side, we find that many different pathways can feasibly contribute to the reaction mechanism, due to the co-existence of multiple cluster isomers, multiple binding geometries of ethylene to the clusters, and multiple accessible C-H bond dissociation paths. Metastable cluster isomers with attached ethylene can have lower barriers to C-H dissociation than the corresponding global minima of the same stoichiometry, and thus contribute substantially to the overall ensemble-average rate of the reaction. It is indeed important that the selectivity of the cluster catalyst is an ensemble property. Pure Pt cluster catalysts usually bind ethylene in the di-

σ mode and efficiently dehydrogenate it, but they can also bind ethylene in the π -mode that discourages dehydrogenation and have high reaction barriers that are within thermal reach to the population. PtSn clusters, on the other hand, mostly favor the π -mode of ethylene binding, favoring desorption instead of dehydrogenation, however, to the extent that some higher energy cluster isomers contribute, they may have thermally-accessible dehydrogenation pathways. DFT calculations combined with statistical analysis confirm that adding Sn to Pt clusters significantly slows down ethylene dehydrogenation.

METHODS

Experimental. Experiments were performed using an instrument described in detail elsewhere,^{3, 5, 61-62} which allows sample creation by size-selected cluster deposition in ultra-high vacuum (UHV), with characterization of physical and chemical properties in *in situ*. The cluster deposition beamline includes a laser vaporization cluster source, ion guides for transport through several differential pumping stages, a quadrupole mass filter for cluster size selection, a valve/lens that isolates the cluster beamline from the UHV system, and a final ion guide that transports ions to the sample, where they are deposited through a 2 mm diameter mask. Samples are mounted via heater wires to a liquid N₂ cryostat that is mounted to a precision manipulator on a rotating “lid” assembly that allows samples to be positioned for sample exchange, cleaning, film growth, cluster deposition, and characterization. Temperature can be controlled in the range from ~120 K to 2100 K.

The UHV section (base pressure 1.0×10^{-10} Torr) includes capabilities for X-ray and UV photoelectron spectroscopy, low energy He⁺ ion scattering spectroscopy, and ion neutralization electron spectroscopy, with analysis area set to 1.1 mm diameter, i.e., smaller than the 2.0 mm

cluster spot. The instrument is also equipped with a differentially pumped mass spectrometer that views the sample through a 2.5 mm diameter aperture in the end of skimmer cone. The cone is surrounded by dosing tubes that are connected to either leak valves or pulsed valves, allowing calibrated continuous or pulsed gas doses with local pressure at the sample position roughly an order of magnitude higher than the increase in background pressure.

A small UHV-compatible antechamber chamber is attached to the main UHV section, isolated by a gate valve. When the valve is opened, the sample can be inserted into the antechamber, and when in position, the two chambers are isolated by a triple differentially pumped seal that mates to the cryostat. This allows the antechamber to be vented for sample exchange, or used for “gassy” processes such as annealing in O₂ or Sn deposition, without exposing the main UHV system to high gas loads.

Model Pt_n/SiO₂/Si(100) and Pt_nSn_x/SiO₂/Si(100) catalysts were prepared on substrates consisting of 10 mm x 14 mm pieces of oxidized Si(100), using a fresh substrate for each experiment. The SiO₂/Si(100) substrates are referred to throughout as “SiO₂” substrates. Substrates were cleaned by annealing at 700 K in 5.0 x 10⁻⁶ Torr O₂ for 20 minutes, followed by 2 min of annealing in UHV. After cleaning, the initial adventitious carbon from air exposure was largely removed, but a small C 1s signal remaining, which we roughly estimated to be ~0.1 ML equivalent. We attempted to remove this residual carbon by sputtering, followed by various annealing protocols in both vacuum and O₂ at temperatures up to 1100 K, and while sputtering does remove the carbon, it creates a large number of defect sites that do not completely anneal away. These create large desorption signals during temperature-programmed desorption (TPD) experiments, interfering with detection of species desorbing from the low coverage of clusters, therefore, we opted to use just O₂ annealing for sample cleaning.

The thickness of the oxidized surface layer was estimated to be 1.1 nm, from modeling³⁹ of the Si^{4+} and Si^0 relative intensities measured by XPS, with photoemission cross sections and asymmetry parameters taken from work by Yeh and Lindau⁶³ and electron effective attenuation lengths calculated using the NIST EAL database program of Powell and Jablonski.⁶⁴ Prior to cluster deposition, the sample cryostat was cooled, and then the sample was flashed to 700 K to drive off any adventitious species that might have adsorbed during cooling. As the sample cooled after the 700 K flash, Pt_n cluster deposition was initiated once the sample reached 300 K and continued as the sample cooled to 180 K. To allow easy exchange of SiO_2 substrates, they are mounted using a tungsten clip to clamp the substrates to a molybdenum backing plate, which is spot welded to Ta heater wires that also act as thermal conductors to the sample cryostat. A type C thermocouple is spot welded to back of the backing plate for temperature measurement.

We chose to study two small clusters, Pt_4 and Pt_7 , both deposited at ~ 1 eV/atom, as measured using retarding potential analysis of the ion beam on the substrate. Deposition was monitored by integrating the Pt_n^+ neutralization current, and for all samples here, the coverage was 1.5×10^{14} Pt atoms/ cm^2 , equivalent to $\sim 10\%$ of a close-packed Pt monolayer. The absolute coverage of clusters is thus $1.5 \times 10^{14}/n$ clusters/ cm^2 , where $n = 4$ or 7 .

The method used to prepare size- and composition-selected PtSn alloy clusters, along with experimental and theoretical characterization of the cluster properties, has been described in detail,² and additional information is given in the Supporting Information. Briefly, size-selected Pt_n ($n = 4, 7$) clusters deposited on SiO_2 substrates were used to “seed” selective Sn deposition via a self-limiting reaction sequence, carried out at 300 K. Pt_n/SiO_2 samples were first exposed to ~ 21000 L of H_2 , which saturates the Pt clusters with H atoms, with essentially no effect on the SiO_2 substrate.⁵ Next, the samples were exposed to ~ 24 L of SnCl_4 vapor, which reacts with

hydrogenated Pt sites, leading to HCl desorption and binding of SnCl_x . The samples were then exposed to an additional 21000 L of H_2 , causing additional HCl desorption, such that <10% of the Cl remained on the cluster surface, along with H and Sn. Finally, the samples were heated briefly to 700 K, desorbing the remaining H and Cl, but with no loss of Sn. ISS showed evidence that heating also allowed the Sn to mix into the Pt cluster, forming an alloy.

Sn deposition was found to be >40 times more efficient on hydrogenated Pt sites than on the SiO_2 support. The cluster Pt:Sn stoichiometry estimated by XPS for the Pt_4 and Pt_7 seed clusters ($\text{Pt}_4\text{Sn}_{3.3}$, $\text{Pt}_7\text{Sn}_{6.3}$) was close to 1:1. It is important to note that the Pt:Sn stoichiometry is unaffected by increasing the reactant exposures,² i.e., the stoichiometry is controlled by the seed cluster size² and the saturation coverage of the ALD reactants on the clusters. Therefore, we expect that the stoichiometry to be reasonably uniform from cluster to cluster, at least as initially prepared.

Desorption and dehydrogenation of ethylene on Pt_n/SiO_2 and $\text{Pt}_n\text{Sn}_x/\text{SiO}_2$ was characterized by C_2D_4 TPD/R. Samples were cooled to 180 K and exposed to 10 L of C_2D_4 , which is roughly twice the dose needed to saturate cluster-associated binding sites that are stable at this temperature.¹ 180 K was chosen to minimize adsorption on the amorphous SiO_2 substrate. After the C_2D_4 exposure, samples were positioned 0.5 mm away from the 2.5 mm diameter aperture that allows desorbing molecules to pass into the ion source of the differentially pumped mass spectrometer (UTI 100C with Extrel electronics). The sample temperature was then ramped at 3 K/sec up to 700 K, while monitoring signal for D_2^+ , H_2O^+ , $^{12}\text{CO}^+$, $^{13}\text{CO}^+$, C_2D_4^+ , H^{35}Cl^+ , $^{12}\text{CO}_2^+$, $^{13}\text{CO}_2^+$, and Cl_2^+ .

CO TPD was used to examine changes in the number and properties of accessible Pt sites accompanying the ethylene TPD experiments. As with the C_2D_4 TPD/R experiments, samples were exposed to 10 L of ^{13}CO at 180 K, then positioned 0.5 mm away from the 2.5 mm diameter

skimmer cone aperture, and the sample temperature was ramped at 3 K/s, to 700 K while monitoring the same masses as above.

After completion of each set of TPD/R experiments, the sample was moved away from the aperture, and the mass spectrometer sensitivity was calibrated by leaking 2.0×10^{-8} Torr of C_2D_4 , D_2 , ^{13}CO , and Ar into the main UHV chamber background. Taking the ionization gauge sensitivity into account, these background pressures create well-defined fluxes of the molecules of interest through the skimmer cone aperture into the mass spectrometer ionization source. Ar was used as a UHV-friendly calibrant for HCl. The masses are similar and should therefore have similar transmission efficiency, and the difference in ionization cross-sections was taken into account using ionization gauge sensitivity factors reported by the gauge manufacturer. This calibration information was used to convert ion signals for C_2D_4^+ , D_2^+ , CO^+ , and H^{35}Cl^+ to the corresponding number of desorbing molecules, based on the assumption that detection efficiency should be similar for molecules desorbing from the surface and effusing from the gas phase. We previously compared calibrations obtained by this method to calibration by desorption of well-defined (2x2)-CO layers from Pd single crystals, and obtained very similar results.^{40, 65} We conservatively estimate that the *absolute* uncertainty in the calibrated desorption signals to be $\sim\pm 50\%$, with uncertainty for comparing experiment to experiment of $\sim\pm 15\%$.

Computational. Global optimization done in this study was performed based on plane wave density functional theory (PW-DFT) calculations with the Vienna Ab initio Simulation Package (VASP)⁶⁶⁻⁶⁹ using projector augmented wave (PAW) potentials⁷⁰ and the PBE⁷¹ functional. Plane waves were chosen based on the kinetic energy cutoff of 400.0 eV. Moreover, the convergence parameters of 10^{-5} (10^{-6}) eV for geometric(electronic) relaxations and Gaussian

smearing with the sigma value of 0.1 eV were used. In order to model the substrate used in the experiment, the chosen SiO₂ slab was previously optimized⁷² elsewhere at the B3LYP/6-31G(d,p)⁷³⁻⁷⁶ level. The obtained cell parameters used in this study are $a = 12.4 \text{ \AA}$, $b = 13.1 \text{ \AA}$, $c = 32.0 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 88^\circ$ which includes the vacuum gap of 10 \AA in the z-direction. Note that the lower half of the slab was kept fixed during the global optimization and only the Γ -point sampling was used to obtain the energy thanks to the fairly large super cell used in this study.

The supported Pt₄ and Pt₄Sn₃ clusters, without and with the adsorbed ethylene, were globally optimized. Larger Pt₇-based clusters were not considered due to the enormous computational expense, additionally given the need for a larger super cell representing the slab. To produce the initial cluster geometries on the surface, we use our in-house code, parallel global optimization and pathway toolkit PGOPT, that automatically generates structures based on the bond length distribution algorithm (BLDA).⁴³ Initial structures for the global optimization calculations should be created, such that they are less prone to encounter Self-Consistent Field (SCF) convergence problems. This can be done by avoiding chemically unfavorable configurations, which results in the reduction of configuration search space and the computational cost of calculation. By constraining the distance of atoms to their closest and second closest neighbors to follow a normal distribution, one can achieve this goal. That is to say, both closest and second closest distances are fitted to normal distribution based on which the initial structures are generated. Subsequently, each generated structure was optimized using DFT and duplicate structures were removed thereafter. The ethylene molecules were placed on the clusters in a multitude of possible orientations and binding sites. Then each structure was optimized using DFT, and duplicates were filtered out. In this study, 200 unique structures were generated and optimized to find the putative global

minimum and the accessible local minima. To take into account the effect of coverage, we also optimized the clusters with two ethylene adsorbed per cluster. A cut-off energy of 0.4 eV was used to select the thermodynamically accessible isomers at relevant temperatures. More detailed discussion about obtaining the vibrational partition functions and corrected Boltzmann population was published before.⁴³ The Bader charge analysis⁷⁷⁻⁸⁰ was used to obtain partial atomic charges. Furthermore, Boltzmann populations were calculated with the assumption that the system can sufficiently equilibrate as

$$P_i = \frac{Z_{elec,i} Z_{trans,i} Z_{vib,i} Z_{rot,i}}{\sum_i Z_i} \approx \frac{g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}}$$

where $Z_{elec,i}$, $Z_{trans,i}$, $Z_{vib,i}$, and $Z_{rot,i}$ are electronic, translational, vibrational, and rotational partition functions, respectively. For the lowest-energy isomers with adsorbed ethylene, which contributed significantly into the respective thermal ensembles, the reaction profile for ethylene dehydrogenation were calculated using climbing image nudged elastic band (CI-NEB) method.⁸¹ Three isomers of each cluster with adsorbed ethylene were chosen and the dissociation of every C-H bond within every adsorbed configuration was tested. All transition states were confirmed by phonon calculations. The distance between the structures (images) in CI-NEB calculations used as reaction coordinate is defined as

$$d_{12} = \sqrt{\frac{1}{N} \sum_i^N (x_{i,1} - x_{i,2})^2 + (y_{i,1} - y_{i,2})^2 + (z_{i,1} - z_{i,2})^2}$$

Rate constants for each pathway were calculated based on harmonic transition state theory.⁸² The ensemble-average rate constant were calculated based on the contribution of each isomer using its Boltzmann population at 700 K:

$$k_{ens} = k_1P_1 + k_2P_2 + k_3P_3$$

, where P_i is the Boltzmann population and k_i ($i = 1-3$) is the sum over all four pathway rate constants obtained from CI-NEB for isomer i .

Finally, *ab initio* MD simulations ran for 10 ps at 700 K with the time step of 1 fs starting from Pt₄/SiO₂ and Pt₄Sn₃/SiO₂ global minimum structures. Nosé–Hoover thermostat was utilized for equilibration during the MD simulations.⁸³

ASSOCIATED CONTENT

Supporting Information Available:

Contains complete sets of C₂D₄ TPD for Pt_n/SiO₂ and Pt_nSn_x/SiO₂, HCl desorption during the first C₂D₄ TPD for Pt_nSn_x/SiO₂, an C 1s XPS regional spectra, the remaining Arrhenius fit plots for Pt₇/SiO₂ and Pt₇Sn_{6.3}/SiO₂, structures of reactants, products, transition states obtained from CI-NEB, Bader charge of all local minima structures along with their Boltzmann populations, Ethylene binding energies obtained from DFT, bond length and bond angle distribution of C₂H₄/Pt₄/SiO₂ and C₂H₄/Pt₄Sn₃/SiO₂ obtained MD simulations, XYZ coordinates of minimum energy pathways obtained from CI-NEB.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENT

This work was supported by the U.S. Air Force Office of Scientific Research under AFOSR Grants FA9550-19-1-0261 and FA9550-16-1-0141.

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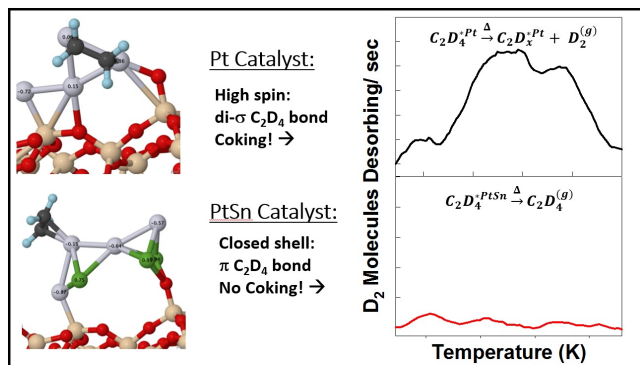
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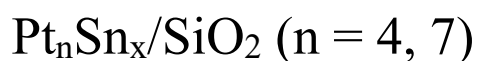
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Coking-Resistant Sub-Nano Dehydrogenation Catalysts:



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Supporting information

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Fig. S1 shows four sequential C₂D₄ TPD runs from Pt₄/SiO₂ (top) and Pt₇/SiO₂ (bottom). As discussed in the main text and shown in **Table 1**, the overall number of available C₂D₄ decreased incrementally with each cycle. Similarly, the amount of liberated D₂ incrementally decreases. C₂D₄ desorption from clean SiO₂ is also shown for each cluster size. There are two distinguishable features for Pt₄, and less so for Pt₇. C₂D₄ desorption begins at the onset of the heat ramp (180 K), peaking around 260 K, and decreasing to baseline by ~500 K. Incremental loss in the number of desorbed C₂D₄(intact) and D₂ molecules is consistent with coke deposition.

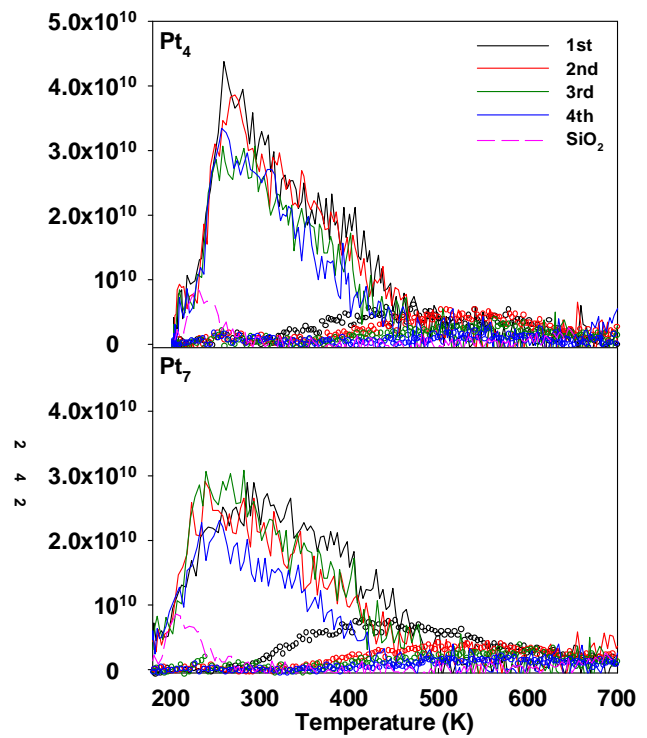


Figure S1. Four sequential C₂D₄ TPD from Pt₄/SiO₂. Intact C₂D₄ is shown as solid lines, and D₂ desorption is shown at hollow symbols. Intact C₂D₄ desorption from clean SiO₂ is also shown in each panel as a dashed pink line.

As was done for **Fig. S1**, four sequential C_2D_4 TPDs were carried out on the $Pt_4Sn_{3.3}/SiO_2$ catalyst. Numbers of C_2D_4 molecules *per* Pt atom are shown in **Table 2** of the manuscript. Results are plotted in in **Fig. S2** along with C_2D_4 desorption from a cluster-free SiO_2 surface that has been exposed to a $H_2/SnCl_4/H_2$ treatment. All four spectra are shown for $Pt_4Sn_{3.3}/SiO_2$ and $Pt_7Sn_{6.3}/SiO_2$, with the D_2 desorption plotted separately on inset plots.

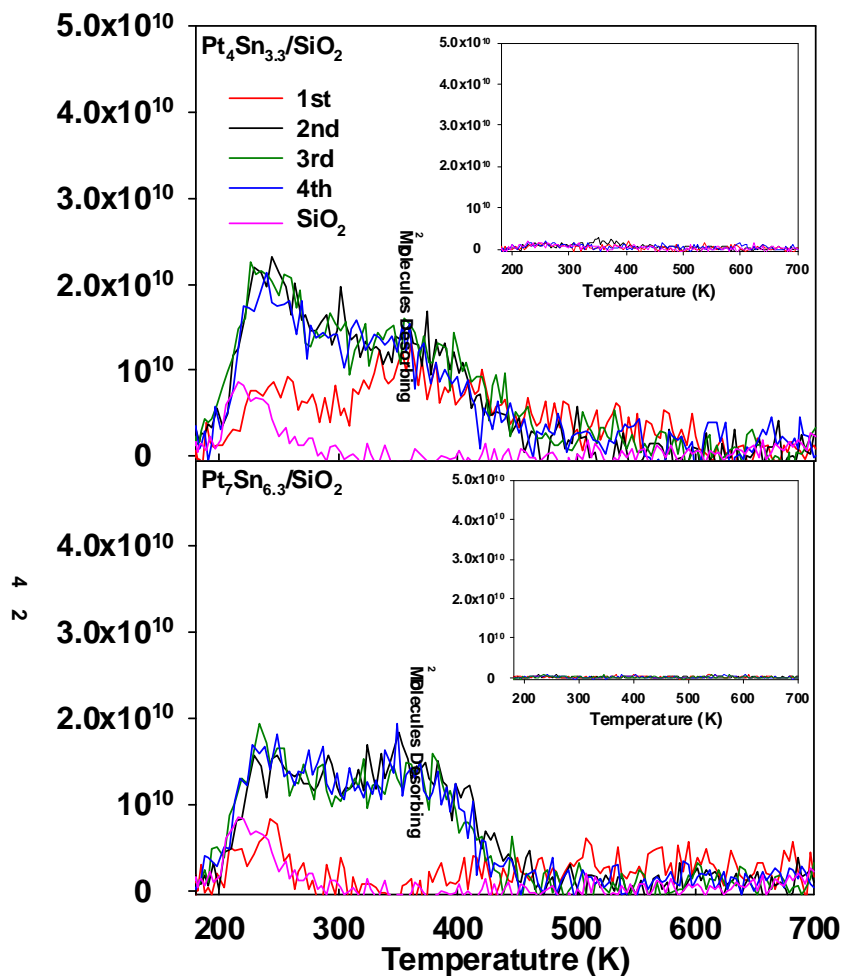


Figure S2. Four sequential desorption spectra of C_2D_4 (solid lines) and D_2 (inset plots) from the first (red) and fourth (blue) C_2D_4 TPD. Each spectra was collected after a 10 L dose of C_2D_4 to Pt_nSn_x/SiO_2 ($n = 4, 7$). C_2D_4 desorption from bare SiO_2 treated with 1 ALD cycle is also plotted (pink line), no D_2 is observed.

Note the anomalous behavior of the first ethylene TPD (red) in **Fig. S2**. This is attributed to the surface being covered with residual H and Cl atoms as a result of the Sn deposition process. The removal of these adsorbates has been described in detail previously, and the mass 36 (HCl) desorption during the first C_2D_4 TPD is shown in **Fig. S3** for both cluster sizes.

Using a method described previously¹⁻², the C₂D₄ thermal desorption spectra can be fit to extract desorption energy distributions by using the first order rate equation:

$$I(t) \propto \frac{-d\theta}{dt} = (\theta(E_{des}) \cdot \nu) e^{\frac{-E_{des}}{kT(t)}}$$

with I(t) being the time-dependent subsequent runs.

C₂D₄ desorption signal, E_{des} the desorption energy, ν the exponential pre-factor, T(t) is the heat ramp, and θ(E_{des}) is the distribution of occupied binding site energies. For all experiments here, a nominal heat ramp rate of 3 K/s was used, but temperature versus time data is always collected during TPD acquisition in order to account for fluctuations in the heating ramp rate, though no corrections were needed. For the fit, a simulated θ(E_{des}) is calculated for each contributing peak and plotted to match the experimentally measured I(t). The greatest source of uncertainty here is the pre-exponential factor, ν. It is not practicable to carry out the series of studies that would be required to estimate ν from the TPD data, and we simply assumed a value of 10¹⁴ s⁻¹, which is in the range of values often used for CO TPD.³⁻⁷ In previous studies², the effect of varying ν between 10¹³ s⁻¹ to 10¹⁵ s⁻¹ was tested, and found to shift the θ(E_{des}) distribution by only ~7%.

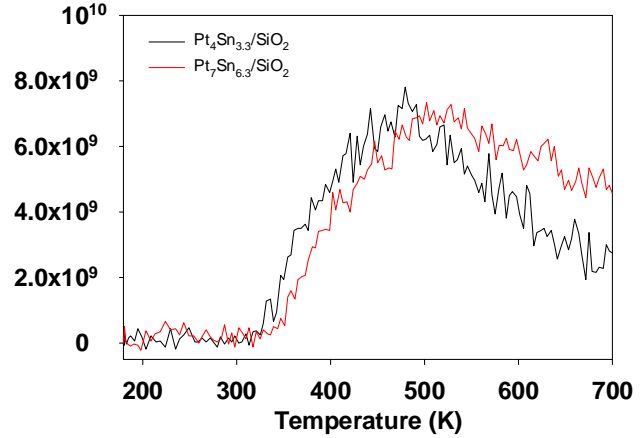


Figure S3. Mass 36 desorption (HCl) during the first C₂D₄ TPD for Pt_nSn_x/SiO₂. No HCl is detected in subsequent runs.

XPS Characterization of Carbon Deposition.

Because the C 1s photoemission cross section is quite small,⁸ and carbon is deposited only on the clusters, it was difficult to quantify carbon deposition for samples of the sort discussed above. To increase the carbon coverage, we prepared Pt₄/SiO₂ and Pt₄Sn_{3.3}/SiO₂ samples with twice the usual cluster coverage, and subjected them to eight sequential C₂D₄ TPD/R runs. The results are compared in **Fig. S4**. A broad C 1s peak is observed for the blank SiO₂ substrate, attributed to adventitious carbon remaining after the substrate was cleaned by annealing in O₂. The binding energy is in the range expected for partially oxidized carbon, as might be expected after annealing in O₂.

For Pt₄/SiO₂ after C₂D₄ TPD/R, this adventitious carbon feature is still present, as expected, but a sharper C 1s feature appears at lower binding energy, which we attribute to carbon deposited on the Pt clusters by C₂D₄ dehydrogenation. Subtracting the contribution from adventitious carbon, the intensity of this low binding energy feature corresponds to eight TPD/R runs having deposited ~1.5 C atom/Pt atom.

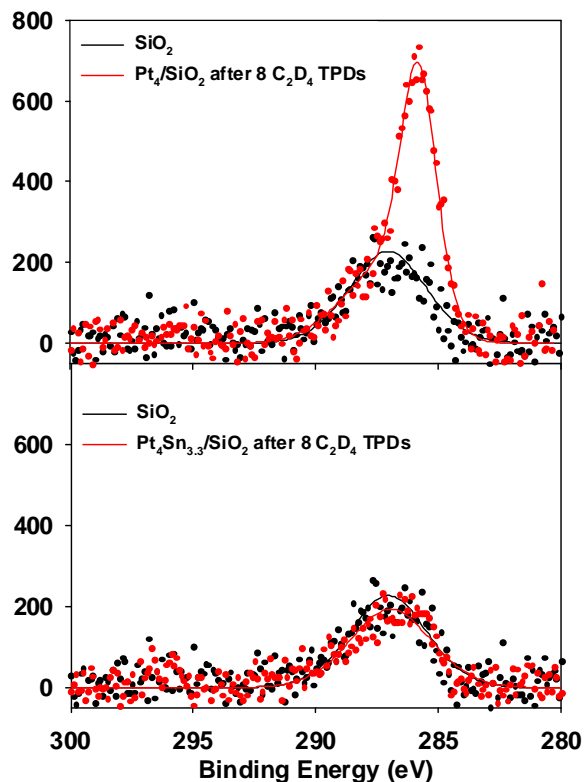


Figure S4. Comparison of C 1s XP spectra for an SiO₂ substrate, a Pt₄/SiO₂ sample, and a Pt₄Sn_{3.3}/SiO₂ sample, subjected to eight sequential C₂D₄ TPD/R runs.

The lower frame of the figure shows analogous data for Pt₄Sn_{3.3}/SiO₂ after eight C₂D₄ TPD runs. No increase in carbon intensity was observed, compared to the SiO₂ substrate, consistent with the TPD/R results showing no significant D₂ desorption from the Sn-alloyed clusters.

Fig. S5 shows the fit for TPD spectra. Here, we use the first C₂D₄ TPD run from Pt₄/SiO₂ as a representative example; this method was carried out for all energy desorption profile plots in this paper. Fits were performed using a two component model, representing low temperature and high temperature feature. Using these fits, the desorption profile was computed and plotted as a function

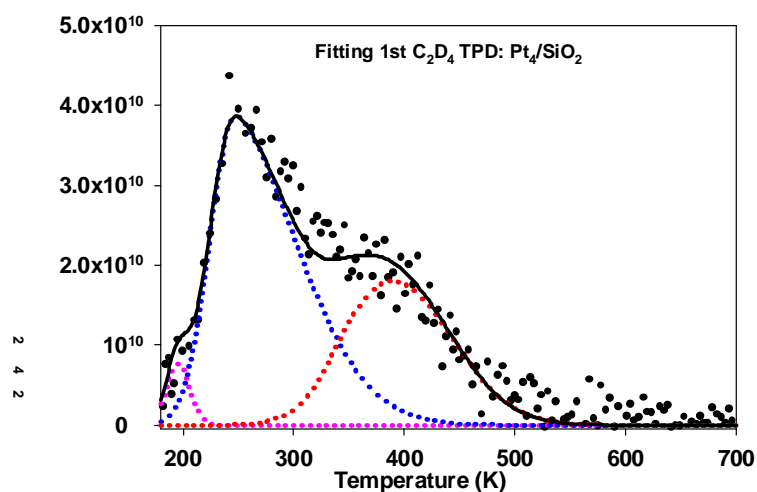


Figure S5. 1st C₂D₄ TPD from Pt₄/SiO₂. The spectrum was fit with low(blue) and high(red) temperature components. The fits can be used to calculate energy desorption profiles.

of binding energy. This model makes the critical assumption of first order desorption kinetics. While we expect some 2nd order behavior for surface-bound C₂D₄, i.e., dissociative adsorption → recombinative desorption, the first order fit was carried out simply to approximate the binding energies for comparison to DFT studies.

Desorption energy distributions for Pt_7/SiO_2 and $\text{Pt}_7\text{Sn}_{6.3}/\text{SiO}_2$ were calculated as described above. Briefly, the first C_2D_4 TPD from Pt_7/SiO_2 was fit with a low and high temperature component and then modeled using a first order kinetics relation. The same was done for the *second* C_2D_4 for the $\text{Pt}_7\text{Sn}_{6.3}/\text{SiO}_2$ sample.

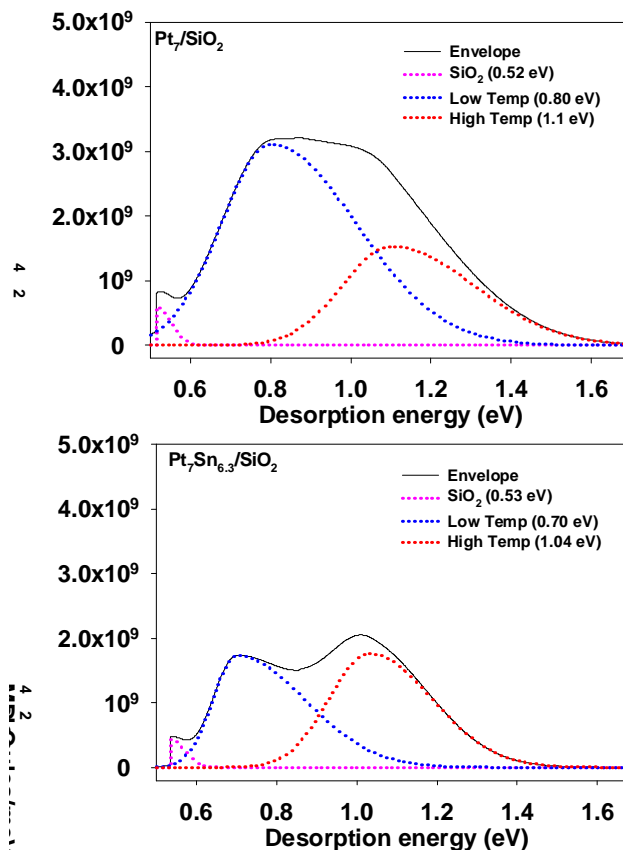


Figure S6. Arrhenius fits for the C_2D_4 TPD from Pt_7/SiO_2 and $\text{Pt}_7\text{Sn}_{6.3}/\text{SiO}_2$ spectra in **Fig. 1**.

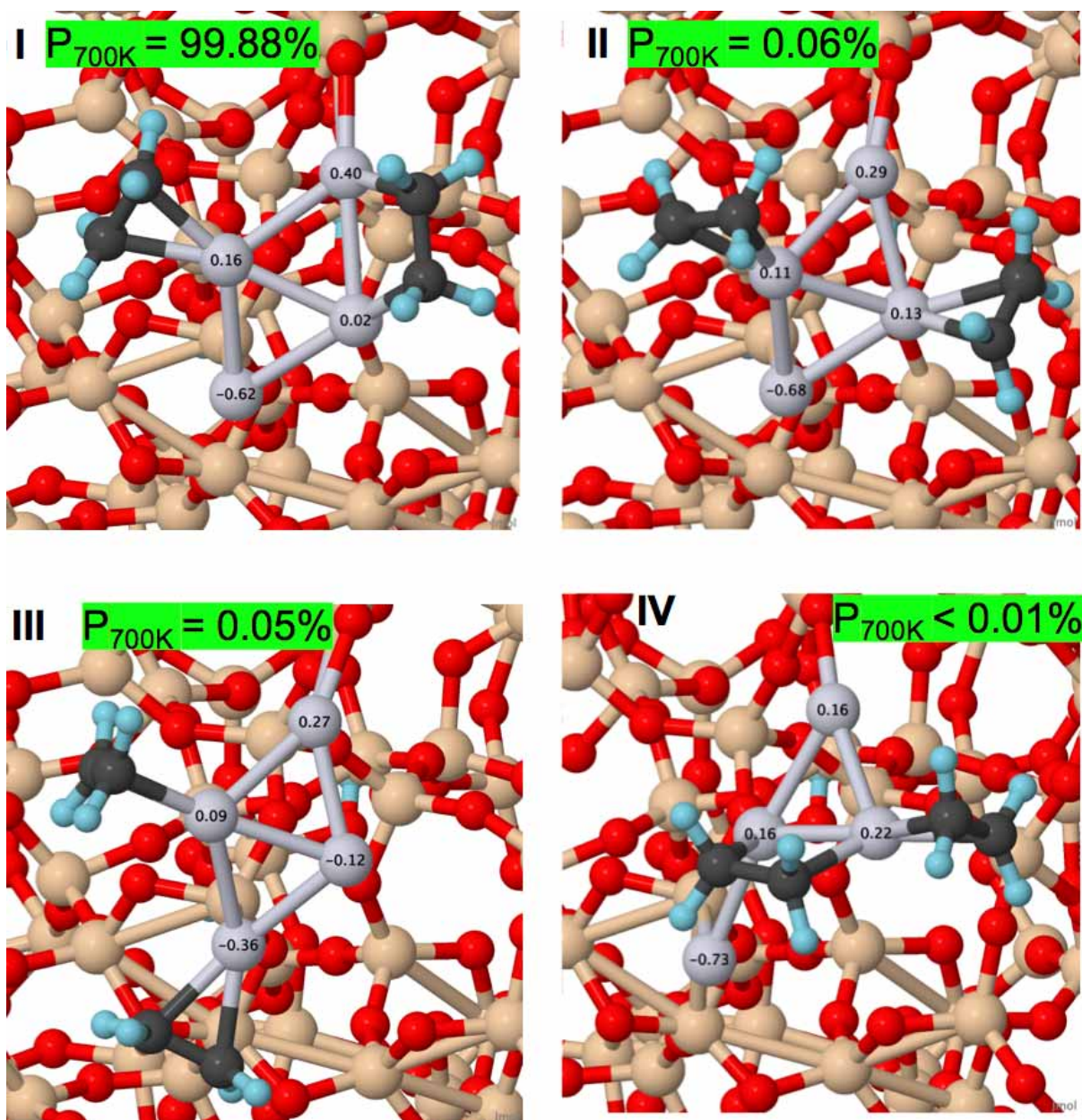


Figure S7. Thermally-accessible geometries of $(C_2H_4)_2/Pt_4/SiO_2$ obtained from global optimization calculations along with their Boltzmann populations at 700 K.

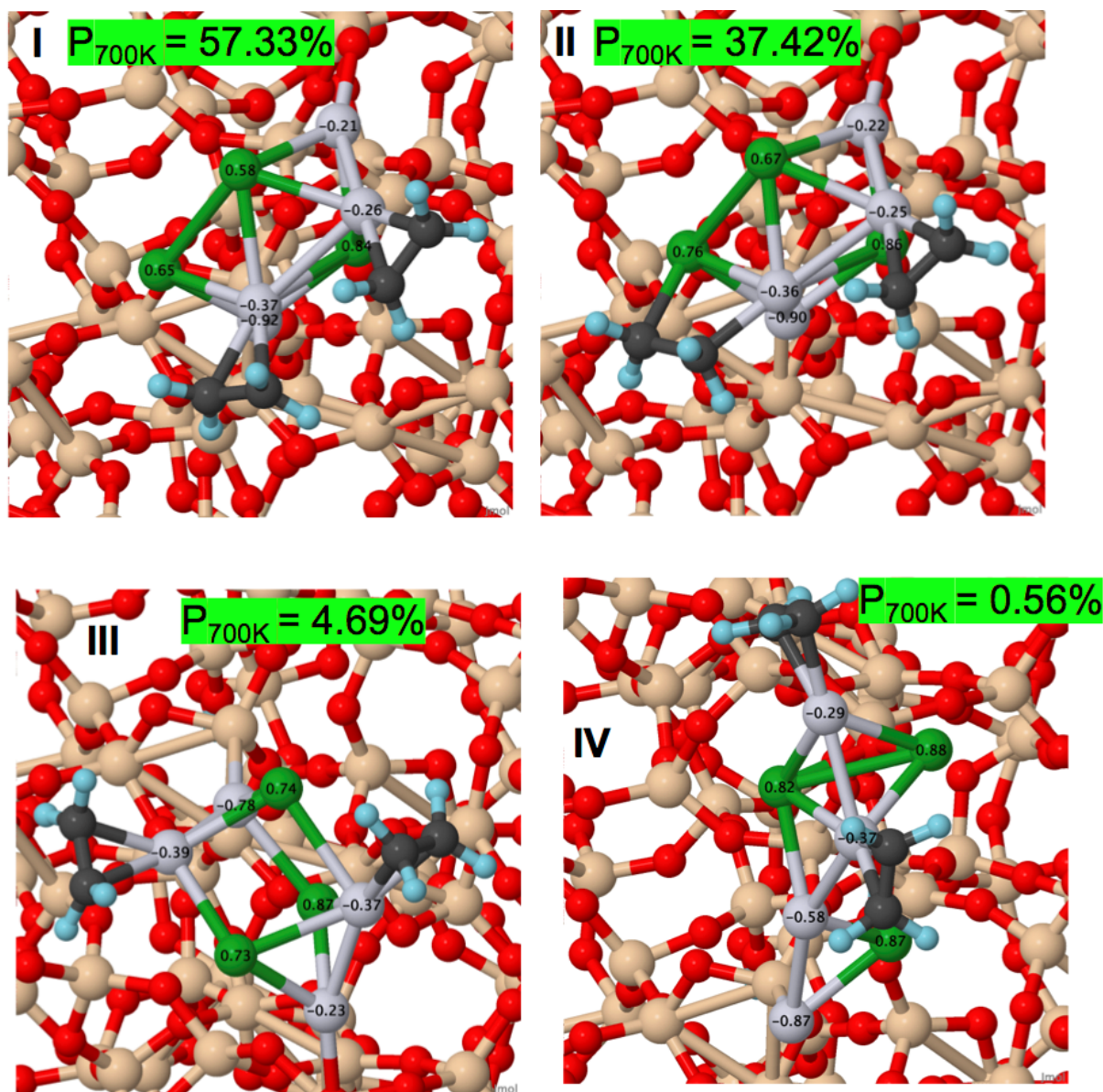


Figure S8. Thermally-accessible geometries of $(\text{C}_2\text{H}_4)_2/\text{Pt}_4\text{Sn}_3/\text{SiO}_2$ obtained from global optimization calculations along with their Boltzmann populations at 700 K. Note that the ensemble is dominated by C_2H_4 π -binding mode.

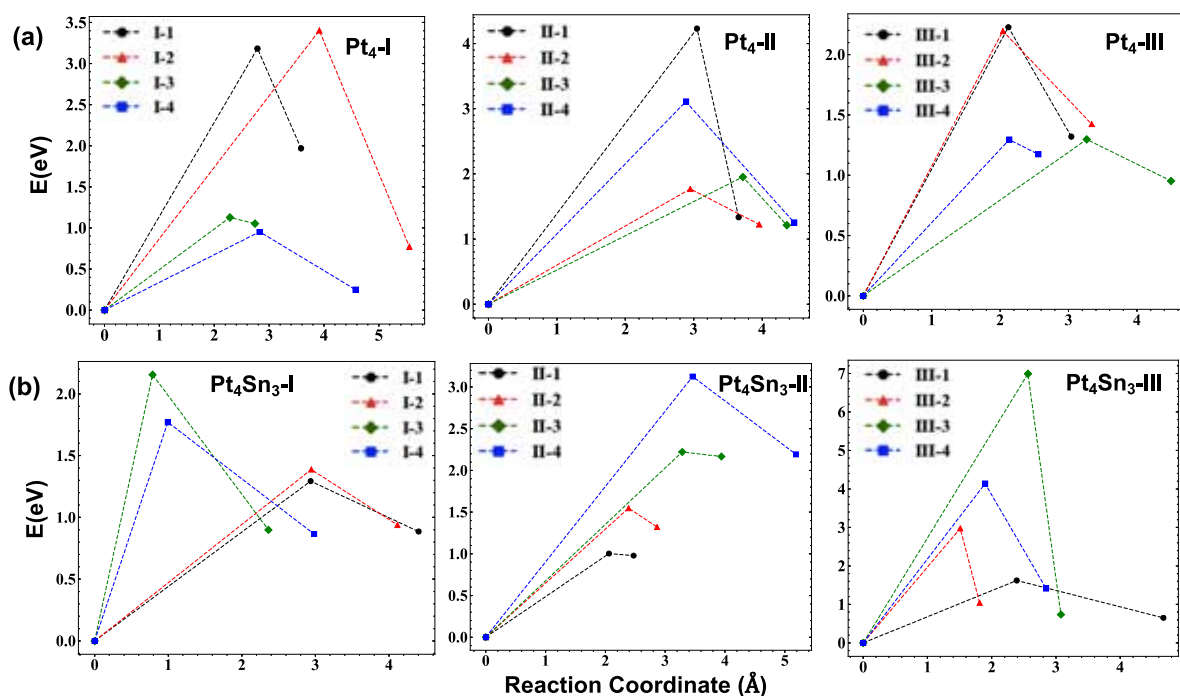


Figure S9. Reaction profiles of breaking C-H bond obtained from CI-NEB calculations for (a) $\text{C}_2\text{H}_4/\text{Pt}_4/\text{SiO}_2$ and (b) $\text{C}_2\text{H}_4/\text{Pt}_4\text{Sn}_3/\text{SiO}_2$. The reaction barrier corresponding to the highest populated $\text{C}_2\text{H}_4/\text{Pt}_4\text{Sn}_3/\text{SiO}_2$ isomer is 0.3 eV higher than that of $\text{C}_2\text{H}_4/\text{Pt}_4/\text{SiO}_2$. The reaction coordinate is defined as the root mean square distance from the reactant, which can be found in the computational methods section.

Table S1. All reaction barriers of $\text{C}_2\text{H}_4/\text{Pt}_4/\text{SiO}_2$ and $\text{C}_2\text{H}_4/\text{Pt}_4\text{Sn}_3/\text{SiO}_2$ obtained from CI-NEB calculations along with their contribution to the final k_{ens} at 700 K.

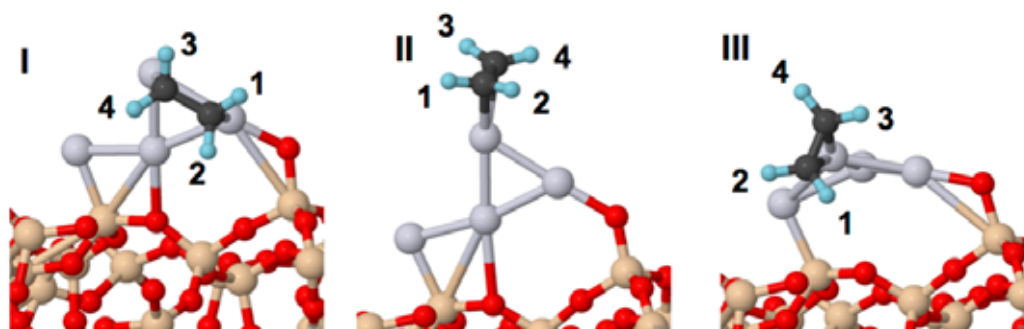
$\text{C}_2\text{H}_4/\text{Pt}_4/\text{SiO}_2$	Barrier (eV)				$P_{700\text{K}}$
	Path-1	Path-2	Path-3	Path-4	
I	0.95	1.13	3.18	3.40	76.71%
II	1.77	1.95	3.11	4.23	23.02%
III	1.29	1.30	2.20	2.23	0.01%
$\text{C}_2\text{H}_4/\text{Pt}_4\text{Sn}_3/\text{SiO}_2$					
I	1.29	1.39	1.77	2.15	69.03%
II	1.00	1.55	2.22	3.12	27.45%
III	1.62	2.97	4.14	6.99	6.70%

Table S2. Charge on the cluster, ethylene binding mode, and Boltzmann population at 700 K obtained for C₂H₄/Pt₄/SiO₂, (C₂H₄)₂/Pt₄/SiO₂, C₂H₄/Pt₄Sn₃/SiO₂, and (C₂H₄)₂/Pt₄Sn₃/SiO₂.

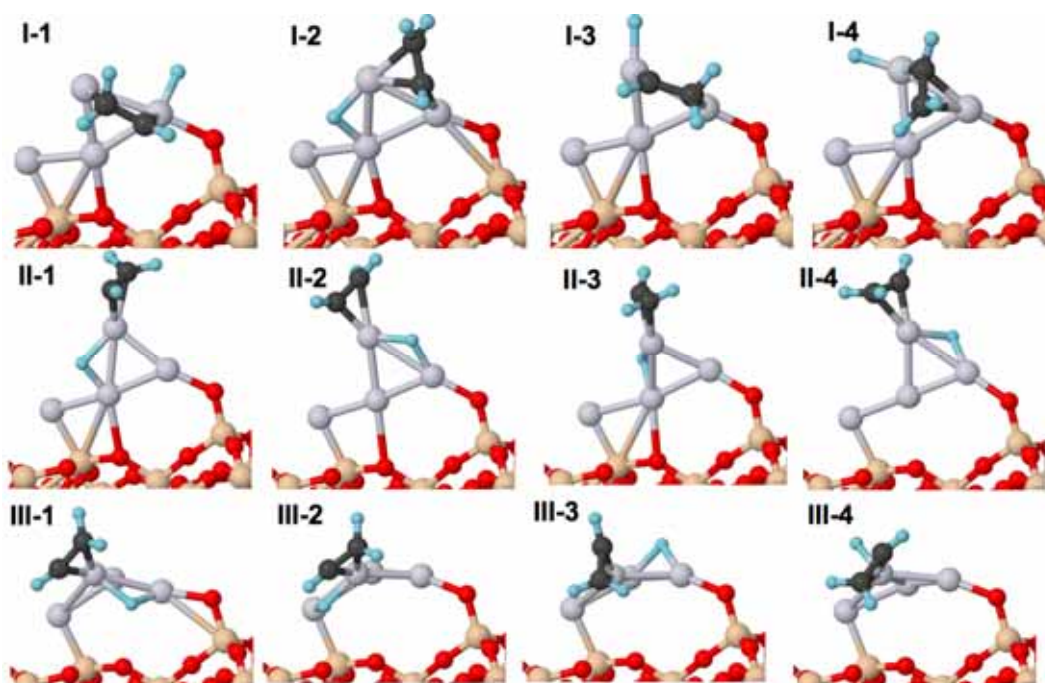
Isomer	Q _{cluster} (e)		C ₂ H ₄ Binding mode		P _{700K}	
C ₂ H ₄ /Pt ₄ Sn _{0.3} /SiO ₂	Pt ₄	Pt ₄ Sn ₃	Pt ₄	Pt ₄ Sn ₃	Pt ₄	Pt ₄ Sn ₃
I	−0.15	0.39	di-σ	π	76.71%	69.03%
II	−0.11	0.46	π	π	23.01%	27.45%
III	−0.10	0.43	π	π	0.25%	2.32%
IV	−0.12	0.50	π	π	0.01%	0.7%
V	−0.12	0.50	di-σ	π	0.01%	0.3%
VI	−0.14	0.32	di-σ	π	<0.01%	0.2%
(C ₂ H ₄) ₂ /Pt ₄ Sn _{0.3} /SiO ₂	Pt ₄	Pt ₄ Sn ₃	Pt ₄	Pt ₄ Sn ₃	Pt ₄	Pt ₄ Sn ₃
I	−0.04	0.31	π, di-σ	π, π	99.88%	57.33%
II	−0.16	0.56	π, π	π, di-σ	0.06%	37.42%
III	−0.11	0.58	π, π	π, π	0.05%	4.69%
IV	−0.19	0.45	π, di-σ	π, π	<0.01%	0.56%

Table S3. Ensemble averaged first and second C₂H₄ binding energies on Pt₄/SiO₂ and Pt₄Sn₃/SiO₂ calculated at 700 K.

Structure	E _{b1} (eV)	E _{b2} (eV)
Pt ₄ /SiO ₂	−1.91	−1.76
Pt ₄ Sn ₃ /SiO ₂	−1.11	−1.04

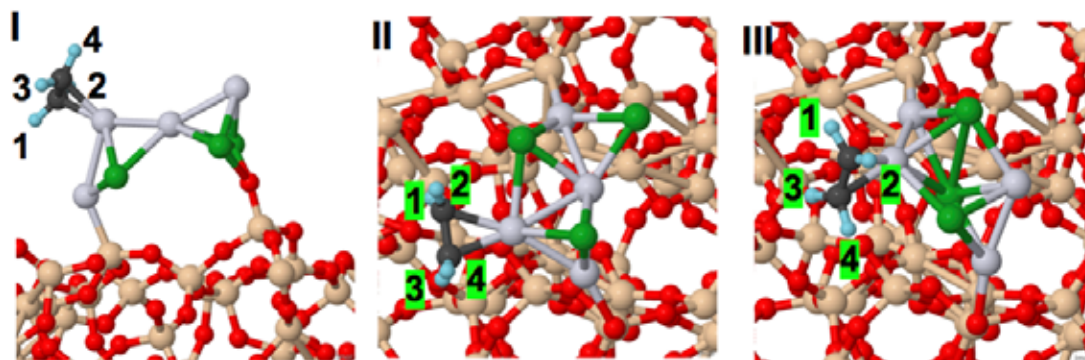


(a)

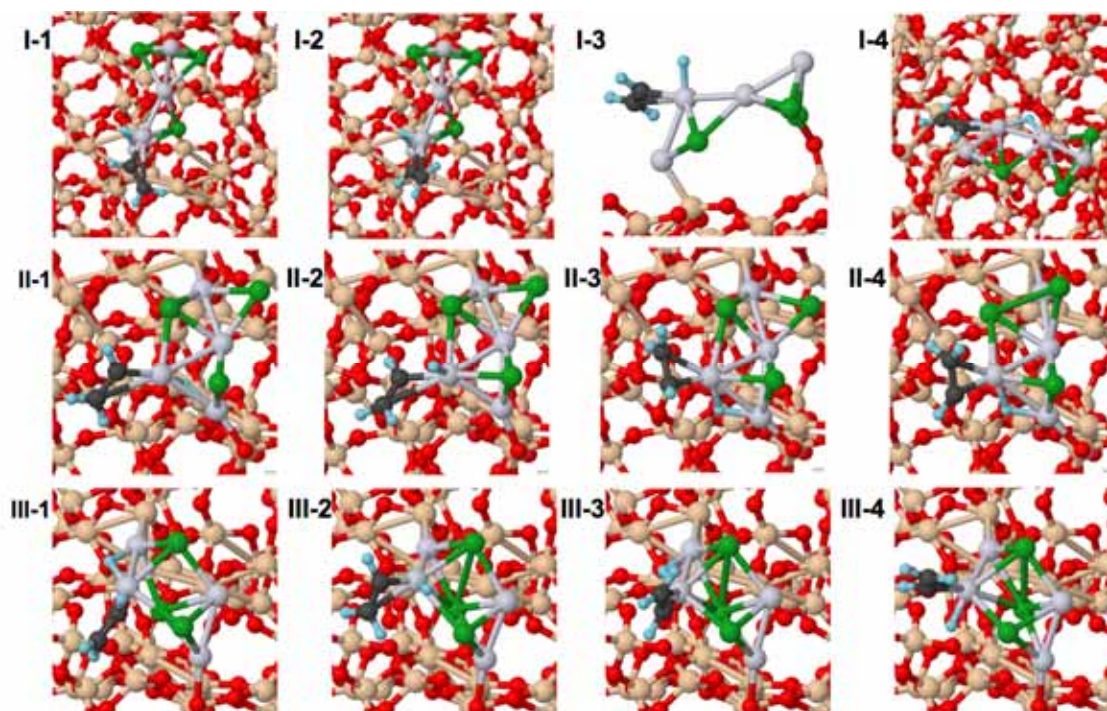


(b)

Figure S10. (a) 3 most populated $\text{C}_2\text{H}_4/\text{Pt}_4/\text{SiO}_2$ isomers used in CI-NEB calculations and (b) all 12 products (4 for each structure) obtained by cleaving every C-H bond in C_2H_4 on Pt_4/SiO_2 .



(a)



(b)

Figure S11. (a) Three most populated $\text{C}_2\text{H}_4/\text{Pt}_4\text{Sn}_3/\text{SiO}_2$ isomers used in CI-NEB calculations and (b) all 12 products (four for each structure) obtained by cleaving every C-H bond in C_2H_4 on $\text{Pt}_4\text{Sn}_3/\text{SiO}_2$.

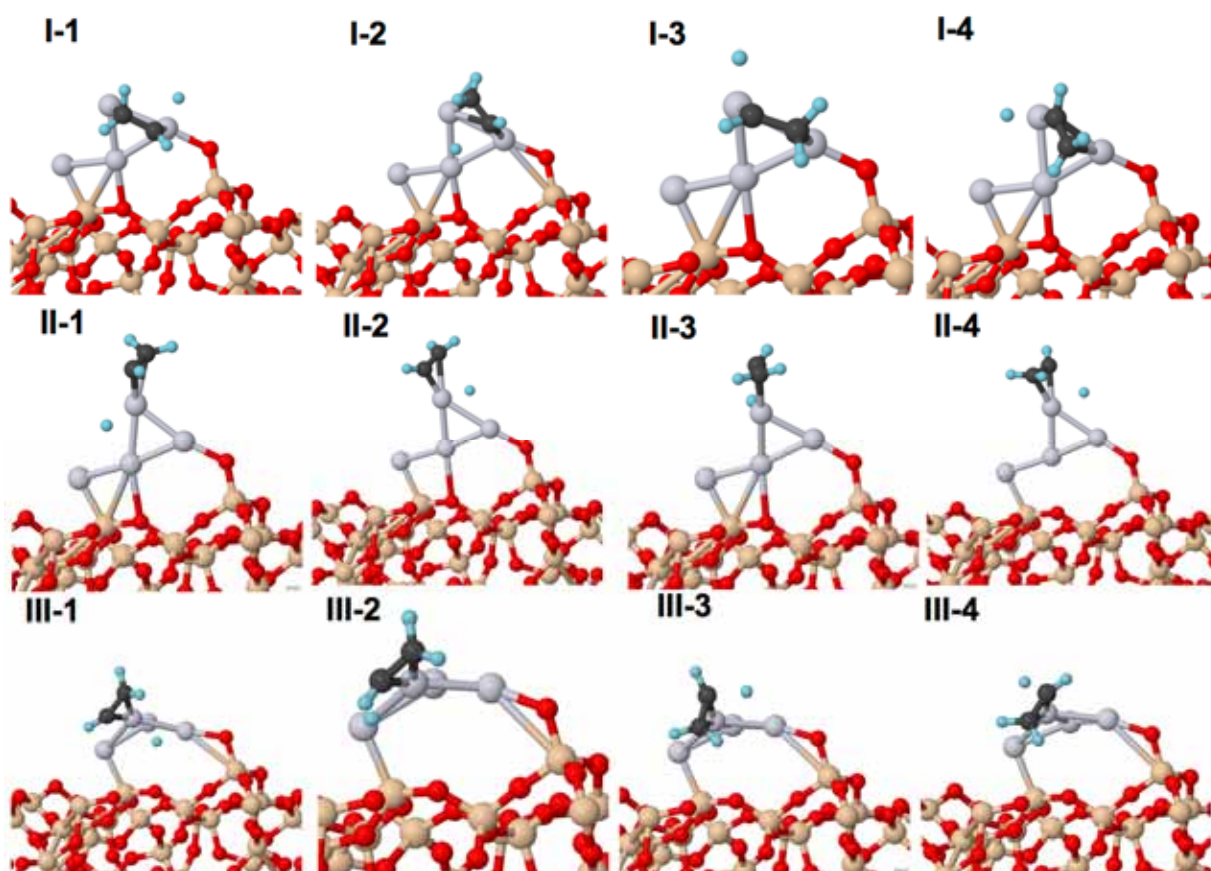


Figure S12. Transition state structures corresponding to all 12 different pathways of C-H bond dissociation on Pt₄/SiO₂ obtained from CI-NEB calculations.

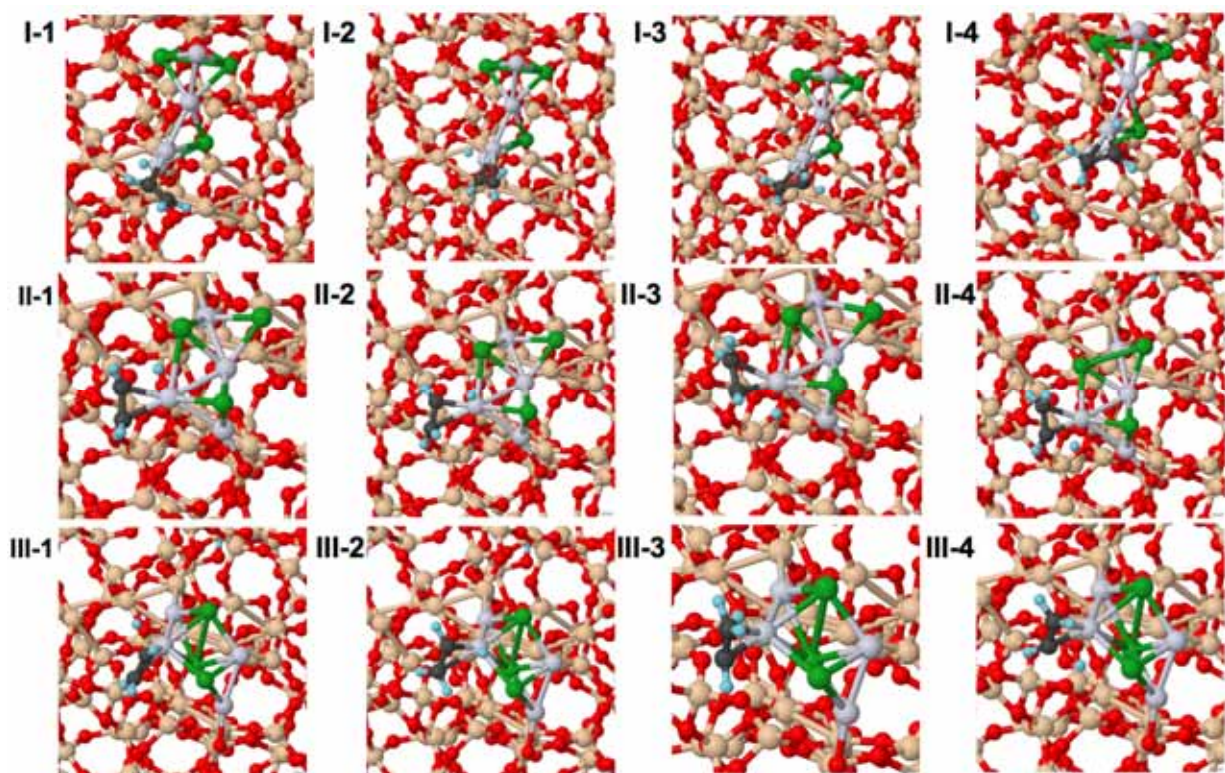


Figure S13. Transition state structures corresponding to all 12 different pathways of C-H bond dissociation on $\text{Pt}_4\text{Sn}_3/\text{SiO}_2$ obtained from CI-NEB calculations.

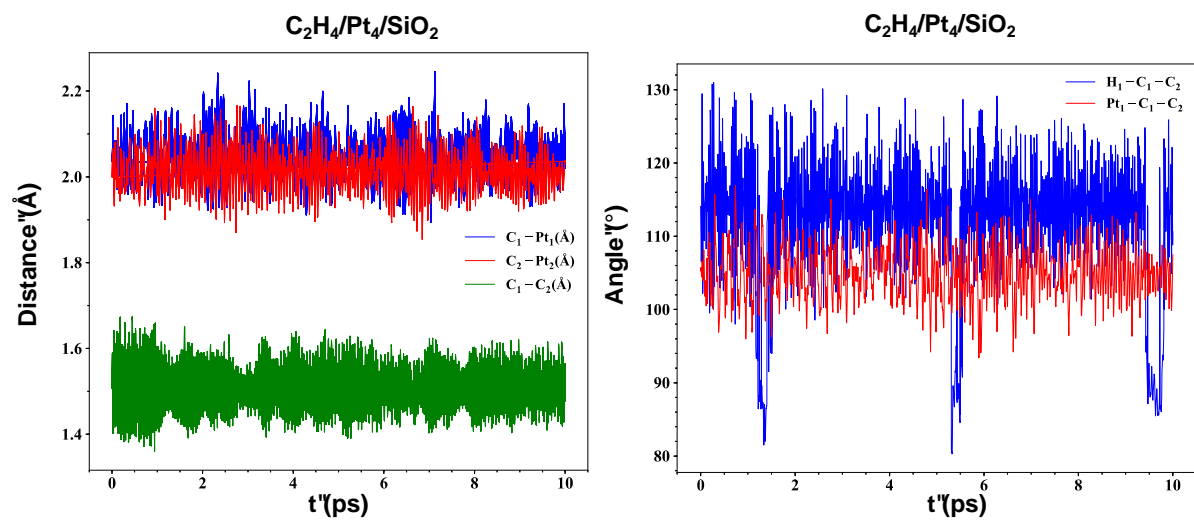


Figure S14. C-C and C-Pt Bond distance, and $\angle HCC$ and $\angle PtCC$ bond angle during the MD simulations of $C_2H_4/Pt_4/SiO_2$. The time step is 1 fs and the total run time is 10 ps.

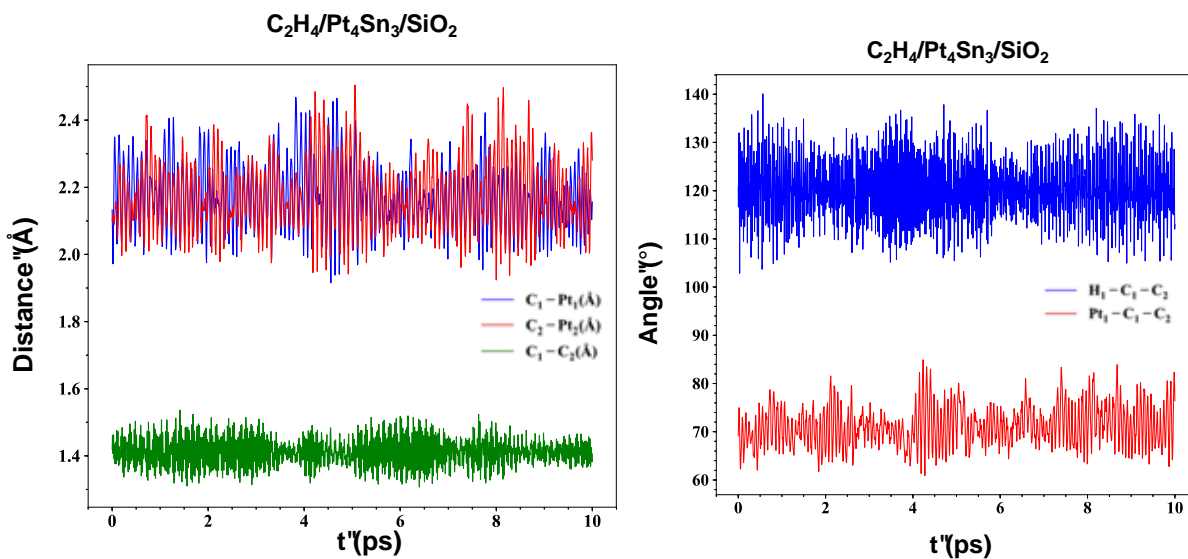


Figure S15. C-C and C-Pt Bond distance, and $\angle\text{HCC}$ and $\angle\text{PtCC}$ bond angle during the MD simulations of $\text{C}_2\text{H}_4/\text{Pt}_4\text{Sn}_3/\text{SiO}_2$. The time step is 1 fs and the total run time is 10 ps.

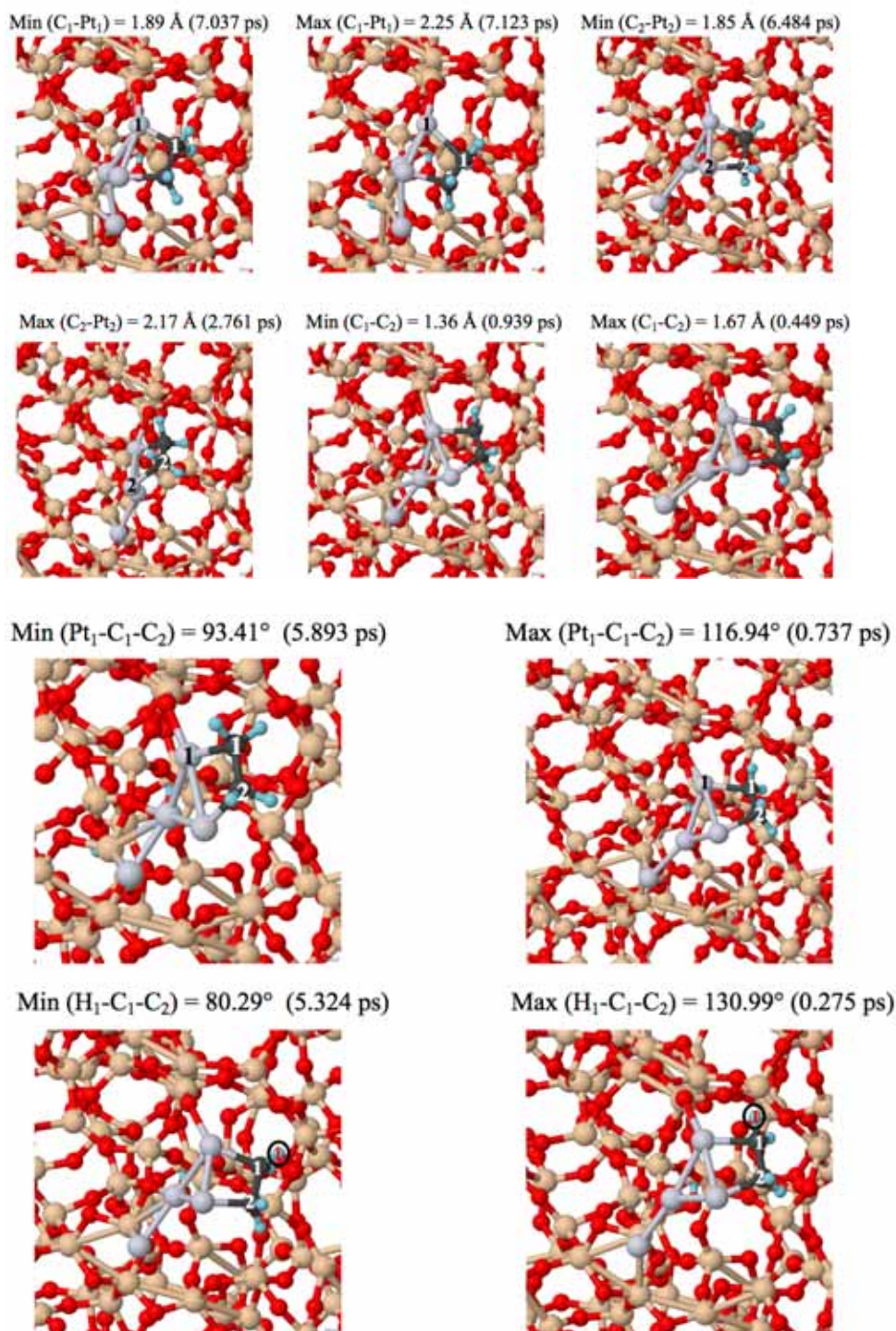


Figure S16. All structures corresponding to an extreme in bond distance or bond angle during the MD simulations of $C_2H_4/Pt_4/SiO_2$ with their corresponding value.

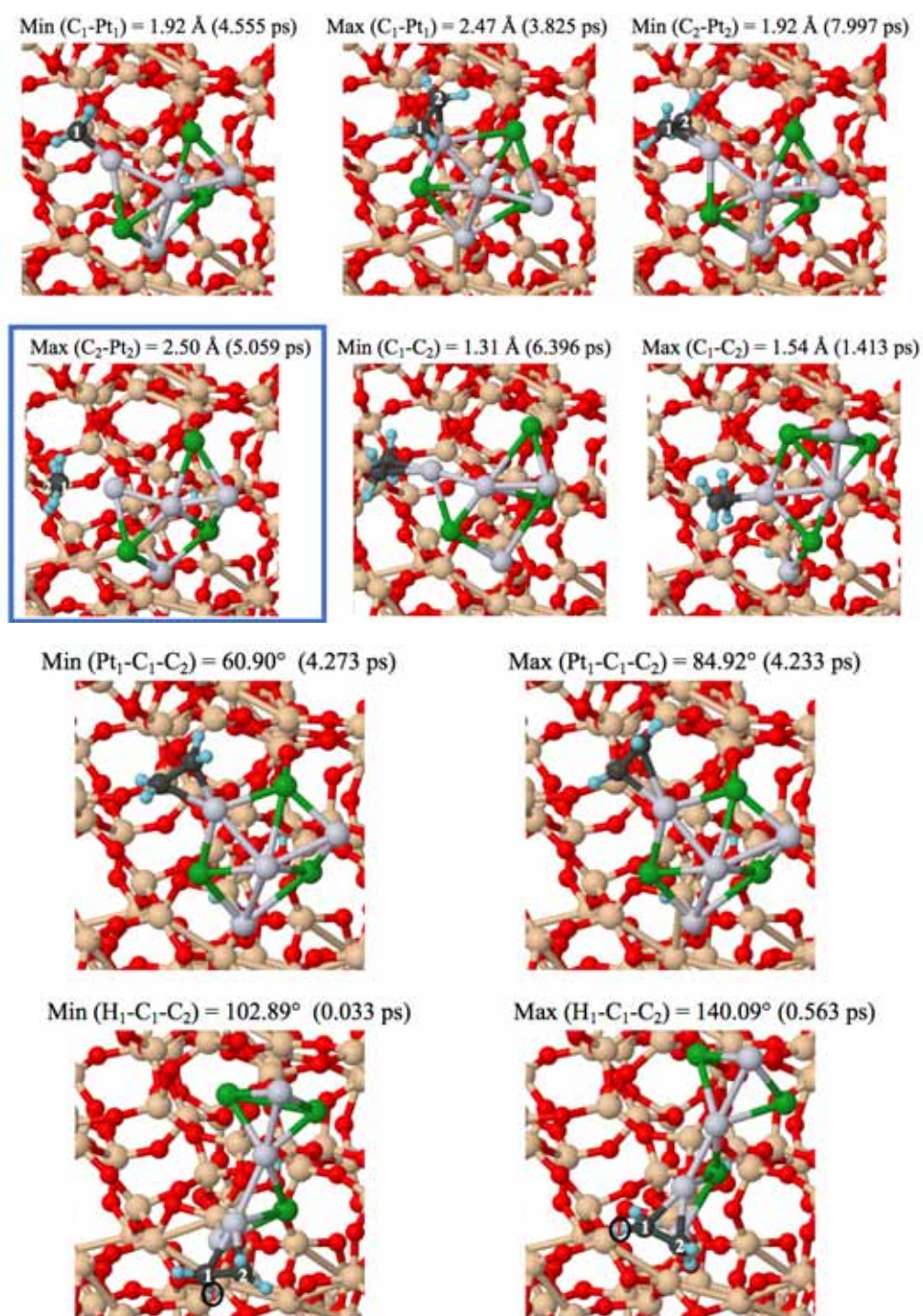


Figure S17. All structures corresponding to an extreme in bond distance or bond angle during the MD simulations of $C_2H_4/Pt_4Sn_3/SiO_2$ with their corresponding value. Note that at 5.059 ps C_2H_4 is almost detached from the cluster.

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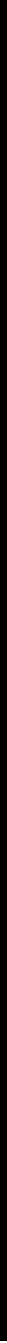
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1. **Introduction**

2. **Background**

3. **Methods**

4. **Results**

5. **Conclusion**

6. **References**

7. **Abbreviations**

8. **Declarations**

9. **Consent to publish**

10. **Consent to participate**

11. **Availability of data and materials**

12. **Competing interests**

13. **Authors' contributions**

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Country	Year	Population (millions)	GDP (billion USD)	Life expectancy (years)	Infant mortality (per 1,000 live births)	Healthcare expenditure (billion USD)	Healthcare workers (thousands)	Healthcare facilities (thousands)	Healthcare services (thousands)
Algeria	2015	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2016	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2017	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2018	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2019	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2020	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2021	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2022	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2023	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2024	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2025	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2026	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2027	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2028	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2029	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2030	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2031	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2032	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2033	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
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Algeria	2036	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
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Algeria	2039	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2040	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2041	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2042	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2043	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2044	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2045	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2046	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2047	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2048	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2049	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2050	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2051	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2052	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2053	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2054	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2055	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2056	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0
Algeria	2057	34.5	110.0	75.0	25.0	1.5	10.0	1.0	1.0

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Year	Country	Population (millions)	GDP (billion USD)	Life expectancy (years)	Infant mortality (per 1,000 live births)	Renewable energy (% of total energy)	Urban population (%)	Internet usage (%)	Gender inequality index	Human development index
2010	USA	310	14,500	78	12	10	80	75	0.25	0.92
2011	USA	312	15,000	78	12	10	80	75	0.25	0.92
2012	USA	314	15,500	78	12	10	80	75	0.25	0.92
2013	USA	316	16,000	78	12	10	80	75	0.25	0.92
2014	USA	318	16,500	78	12	10	80	75	0.25	0.92
2015	USA	320	17,000	78	12	10	80	75	0.25	0.92
2016	USA	322	17,500	78	12	10	80	75	0.25	0.92
2017	USA	324	18,000	78	12	10	80	75	0.25	0.92
2018	USA	326	18,500	78	12	10	80	75	0.25	0.92
2019	USA	328	19,000	78	12	10	80	75	0.25	0.92
2020	USA	330	19,500	78	12	10	80	75	0.25	0.92
2010	China	1,370	5,900	75	30	15	60	40	0.45	0.70
2011	China	1,375	6,000	75	30	15	60	40	0.45	0.70
2012	China	1,380	6,100	75	30	15	60	40	0.45	0.70
2013	China	1,385	6,200	75	30	15	60	40	0.45	0.70
2014	China	1,390	6,300	75	30	15	60	40	0.45	0.70
2015	China	1,395	6,400	75	30	15	60	40	0.45	0.70
2016	China	1,400	6,500	75	30	15	60	40	0.45	0.70
2017	China	1,405	6,600	75	30	15	60	40	0.45	0.70
2018	China	1,410	6,700	75	30	15	60	40	0.45	0.70
2019	China	1,415	6,800	75	30	15	60	40	0.45	0.70
2020	China	1,420	6,900	75	30	15	60	40	0.45	0.70
2010	India	1,100	1,500	68	100	5	40	20	0.60	0.55
2011	India	1,110	1,550	68	100	5	40	20	0.60	0.55
2012	India	1,120	1,600	68	100	5	40	20	0.60	0.55
2013	India	1,130	1,650	68	100	5	40	20	0.60	0.55
2014	India	1,140	1,700	68	100	5	40	20	0.60	0.55
2015	India	1,150	1,750	68	100	5	40	20	0.60	0.55
2016	India	1,160	1,800	68	100	5	40	20	0.60	0.55
2017	India	1,170	1,850	68	100	5	40	20	0.60	0.55
2018	India	1,180	1,900	68	100	5	40	20	0.60	0.55
2019	India	1,190	1,950	68	100	5	40	20	0.60	0.55
2020	India	1,200	2,000	68	100	5	40	20	0.60	0.55
2010	Germany	82	3,500	80	8	20	90	90	0.15	0.85
2011	Germany	82	3,500	80	8	20	90	90	0.15	0.85
2012	Germany	82	3,500	80	8	20	90	90	0.15	0.85
2013	Germany	82	3,500	80	8	20	90	90	0.15	0.85
2014	Germany	82	3,500	80	8	20	90	90	0.15	0.85
2015	Germany	82	3,500	80	8	20	90	90	0.15	0.85
2016	Germany	82	3,500	80	8	20	90	90	0.15	0.85
2017	Germany	82	3,500	80	8	20	90	90	0.15	0.85
2018	Germany	82	3,500	80	8	20	90	90	0.15	0.85
2019	Germany	82	3,500	80	8	20	90	90	0.15	0.85
2020										

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Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360	2361	2362	2363	2364	2365	2366	2367	2368	2369	2370	2371	2372	2373	2374	2375	2376	2377	2378	2379	2380	2381	2382	2383	2384	2385	2386	2387	2388	2389	2390	2391	2392	2393	2394	2395	2396	2397	2398	2399	2400	2401	2402	2403	2404	2405	2406	2407	2408	2409	2410	2411	2412	2413	2414	2415	2416	2417	2418	2419	2420	2421	2422	2423	2424	2425	2426	2427	2428	2429	2430	2431	2432	2433	2434	2435	2436	2437	2438	2439	2440	2441	2442
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Country	Year	Population (millions)	GDP (billion USD)	Life expectancy (years)	Infant mortality (per 1,000 live births)	Unemployment (%)	Urban population (%)	Healthcare expenditure (USD per capita)	Renewable energy consumption (%)	Internet usage (%)	Gender inequality index	Human development index
Algeria	2018	35.0	170.0	75.0	20.0	10.0	60.0	100.0	1.0	50.0	0.60	0.70
Algeria	2019	35.5	175.0	75.5	19.5	10.5	60.5	105.0	1.0	50.5	0.60	0.71
Algeria	2020	36.0	180.0	76.0	19.0	11.0	61.0	110.0	1.0	51.0	0.60	0.72
Algeria	2021	36.5	185.0	76.5	18.5	11.5	61.5	115.0	1.0	51.5	0.60	0.73
Algeria	2022	37.0	190.0	77.0	18.0	12.0	62.0	120.0	1.0	52.0	0.60	0.74
Algeria	2023	37.5	195.0	77.5	17.5	12.5	62.5	125.0	1.0	52.5	0.60	0.75
Algeria	2024	38.0	200.0	78.0	17.0	13.0	63.0	130.0	1.0	53.0	0.60	0.76
Algeria	2025	38.5	205.0	78.5	16.5	13.5	63.5	135.0	1.0	53.5	0.60	0.77
Algeria	2026	39.0	210.0	79.0	16.0	14.0	64.0	140.0	1.0	54.0	0.60	0.78
Algeria	2027	39.5	215.0	79.5	15.5	14.5	64.5	145.0	1.0	54.5	0.60	0.79
Algeria	2028	40.0	220.0	80.0	15.0	15.0	65.0	150.0	1.0	55.0	0.60	0.80
Algeria	2029	40.5	225.0	80.5	14.5	15.5	65.5	155.0	1.0	55.5	0.60	0.81
Algeria	2030	41.0	230.0	81.0	14.0	16.0	66.0	160.0	1.0	56.0	0.60	0.82
Algeria	2031	41.5	235.0	81.5	13.5	16.5	66.5	165.0	1.0	56.5	0.60	0.83
Algeria	2032	42.0	240.0	82.0	13.0	17.0	67.0	170.0	1.0	57.0	0.60	0.84
Algeria	2033	42.5	245.0	82.5	12.5	17.5	67.5	175.0	1.0	57.5	0.60	0.85
Algeria	2034	43.0	250.0	83.0	12.0	18.0	68.0	180.0	1.0	58.0	0.60	0.86
Algeria	2035	43.5	255.0	83.5	11.5	18.5	68.5	185.0	1.0	58.5	0.60	0.87
Algeria	2036	44.0	260.0	84.0	11.0	19.0	69.0	190.0	1.0	59.0	0.60	0.88
Algeria	2037	44.5	265.0	84.5	10.5	19.5	69.5	195.0	1.0	59.5	0.60	0.89
Algeria	2038	45.0	270.0	85.0	10.0	20.0	70.0	200.0	1.0	60.0	0.60	0.90
Algeria	2039	45.5	275.0	85.5	9.5	20.5	70.5	205.0	1.0	60.5	0.60	0.91
Algeria	2040	46.0	280.0	86.0	9.0	21.0	71.0	210.0	1.0	61.0	0.60	0.92
Algeria	2041	46.5	285.0	86.5	8.5	21.5	71.5	215.0	1.0	61.5	0.60	0.93
Algeria	2042	47.0	290.0	87.0	8.0	22.0	72.0	220.0	1.0	62.0	0.60	0.94
Algeria	2043	47.5	295.0	87.5	7.5	22.5	72.5	225.0	1.0	62.5	0.60	0.95
Algeria	2044	48.0	300.0	88.0	7.0	23.0	73.0	230.0	1.0	63.0	0.60	0.96
Algeria	2045	48.5	305.0	88.5	6.5	23.5	73.5	235.0	1.0	63.5	0.60	0.97
Algeria	2046	49.0	310.0	89.0	6.0	24.0	74.0	240.0	1.0	64.0	0.60	0.98
Algeria	2047	49.5	315.0	89.5	5.5	24.5	74.5	245.0	1.0	64.5	0.60	0.99
Algeria	2048	50.0	320.0	90.0	5.0	25.0	75.0	250.0	1.0	65.0	0.60	1.00
Algeria	2049	50.5	325.0	90.5	4.5	25.5	75.5	255.0	1.0	65.5	0.60	1.01
Algeria	2050	51.0	330.0	91.0								

Country	Year	Population (millions)	GDP (billion USD)	Life expectancy (years)	Infant mortality (per 1,000 live births)	Unemployment (%)	Urban population (%)	Healthcare expenditure (billion USD)	Renewable energy consumption (%)	Internet usage (%)	Gender inequality index	Human Development Index
Algeria	2019	4.0	210	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2018	4.0	200	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2017	4.0	190	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2016	4.0	180	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2015	4.0	170	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2014	4.0	160	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2013	4.0	150	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2012	4.0	140	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2011	4.0	130	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2010	4.0	120	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2009	4.0	110	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2008	4.0	100	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2007	4.0	90	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2006	4.0	80	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2005	4.0	70	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2004	4.0	60	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2003	4.0	50	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2002	4.0	40	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2001	4.0	30	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	2000	4.0	20	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1999	4.0	10	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1998	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1997	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1996	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1995	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1994	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1993	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1992	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1991	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1990	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1989	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1988	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1987	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1986	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1985	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1984	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1983	4.0	5	75	25	10	60	1.5	15	50	0.65	0.70
Algeria	1982	4.0	5	75	25	10	60					

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Year	Country	Population (millions)	GDP (billion USD)	Life expectancy (years)	Infant mortality (per 1,000 live births)	Unemployment (%)	Urban population (%)	Healthcare expenditure (billion USD)	Renewable energy consumption (%)	Internet usage (%)	Gender inequality index
2010	USA	310	14,980	78.4	12.1	4.6	80.9	2,540	10.1	78.1	0.62
2011	USA	312	15,360	78.6	11.9	4.5	81.1	2,600	10.2	78.5	0.61
2012	USA	314	15,740	78.8	11.7	4.4	81.3	2,660	10.3	78.9	0.60
2013	USA	316	16,120	79.0	11.5	4.3	81.5	2,720	10.4	79.3	0.59
2014	USA	318	16,500	79.2	11.3	4.2	81.7	2,780	10.5	79.7	0.58
2015	USA	320	16,880	79.4	11.1	4.1	81.9	2,840	10.6	80.1	0.57
2016	USA	322	17,260	79.6	10.9	4.0	82.1	2,900	10.7	80.5	0.56
2017	USA	324	17,640	79.8	10.7	3.9	82.3	2,960	10.8	80.9	0.55
2018	USA	326	18,020	80.0	10.5	3.8	82.5	3,020	10.9	81.3	0.54
2019	USA	328	18,400	80.2	10.3	3.7	82.7	3,080	11.0	81.7	0.53
2020	USA	330	18,780	80.4	10.1	3.6	82.9	3,140	11.1	82.1	0.52
2010	China	1,370	5,880	74.7	21.4	13.2	52.8	1,120	1.2	45.2	0.75
2011	China	1,375	6,160	75.0	20.8	13.0	53.1	1,160	1.3	45.8	0.74
2012	China	1,380	6,440	75.3	20.2	12.8	53.4	1,200	1.4	46.4	0.73
2013	China	1,385	6,720	75.6	19.6	12.6	53.7	1,240	1.5	47.0	0.72
2014	China	1,390	7,000	75.9	19.0	12.4	54.0	1,280	1.6	47.6	0.71
2015	China	1,395	7,280	76.2	18.4	12.2	54.3	1,320	1.7	48.2	0.70
2016	China	1,400	7,560	76.5	17.8	12.0	54.6	1,360	1.8	48.8	0.69
2017	China	1,405	7,840	76.8	17.2	11.8	54.9	1,400	1.9	49.4	0.68
2018	China	1,410	8,120	77.1	16.6	11.6	55.2	1,440	2.0	50.0	0.67
2019	China	1,415	8,400	77.4	16.0	11.4	55.5	1,480	2.1	50.6	0.66
2020	China	1,420	8,680	77.7	15.4	11.2	55.8	1,520	2.2	51.2	0.65
2010	India	1,100	1,920	69.4	30.1	19.5	31.2	480	0.8	25.1	0.88
2011	India	1,110	2,040	69.8	29.2	19.2	31.8	500	0.9	25.8	0.87
2012	India	1,120	2,160	70.2	28.3	19.0	32.4	520	1.0	26.5	0.86
2013	India	1,130	2,280	70.6	27.4	18.8	33.0	540	1.1	27.2	0.85
2014	India	1,140	2,400	71.0	26.5	18.6	33.6	560	1.2	27.9	0.84
2015	India	1,150	2,520	71.4	25.6	18.4	34.2	580	1.3	28.6	0.83
2016	India	1,160	2,640	71.8	24.7	18.2	34.8	600	1.4	29.3	0.82
2017	India	1,170	2,760	72.2	23.8	18.0	35.4	620	1.5	30.0	0.81
2018	India	1,180	2,880	72.6	22.9	17.8	36.0	640	1.6	30.7	0.80
2019	India	1,190	3,000	73.0	22.0	17.6	36.6	660	1.7	31.4	0.79
2020	India	1,200	3,120	73.4	21.1	17.4	37.2	680	1.8	32.1	0.78
2010	Germany	82	3,560	80.6	7.1	5.1	73.1	1,120	18.2	85.1	0.45
2011	Germany	82	3,600	80.7	7.0	5.0	73.2	1,140	18.3	85.2	0.45
2012	Germany	82	3,640	80.8	6.9	4.9	73.3				

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Year	Country	Population (millions)	GDP (billions of USD)	Life expectancy (years)	Infant mortality rate (per 1,000 live births)	Urban population (%)	Renewable energy consumption (%)	Forest area (thousands of hectares)	CO2 emissions (thousands of metric tons)	Internet usage (%)	Mobile phone usage (%)	Healthcare expenditure (USD per capita)	Education expenditure (USD per capita)	Research and development expenditure (USD per capita)	Gender inequality index	Corruption index	Human development index	World Bank ID
2015	USA	365	18.5	78.5	10.5	81	12	600	15.5	85	95	3,500	1,200	1,500	0.65	70	0.92	US
2015	China	1,370	12.0	76.5	23.5	54	15	1,200	10.0	55	85	2,500	800	1,000	0.75	65	0.72	CH
2015	India	1,250	2.0	73.5	30.5	31	10	1,500	2.0	35	75	1,000	400	500	0.60	55	0.65	IN
2015	Germany	82	4.0	81.5	7.5	73	25	100	8.0	90	98	4,000	1,500	2,000	0.85	80	0.95	DE
2015	Japan	127	5.0	84.5	6.5	94	20	150	12.0	95	99	4,500	1,800	2,500	0.90	85	0.98	JP
2015	UK	64	3.0	81.5	8.5	89	22	120	7.0	92	97	3,800	1,400	1,800	0.88	78	0.94	GB
2015	France	67	2.8	82.5	9.5	91	21	110	6.5	93	98	3,900	1,500	1,900	0.87	79	0.96	FR
2015	Canada	36	2.0	82.5	7.5	82	28	130	9.0	94	99	4,200	1,700	2,200	0.91	82	0.97	CA
2015	Italy	61	2.5	83.5	8.5	72	23	140	5.5	91	97	3,700	1,400	1,700	0.86	77	0.93	IT
2015	Spain	46	2.0	83.5	9.5	65	24	160	4.5	90	96	3,600	1,300	1,600	0.84	76	0.92	ES
2015	South Korea	51	1.7	83.5	7.5	85	26	170	11.0	96	99	4,300	1,800	2,300	0.92	83	0.98	KR
2015	Sweden	10	0.5	83.5	6.5	88	35	180	13.0	97	99	4,400	1,900	2,400	0.93	84	0.99	SE
2015	Norway	5	0.4	83.5	6.5	87	36	190	14.0	98	99	4,500	2,000	2,500	0.94	85	1.00	NO
2015	Denmark	5.6	0.4	83.5	6.5	86	37	200	15.0	98	99	4,600	2,100	2,600	0.95	86	1.00	DK
2015	Netherlands	17	0.5	82.5	7.5	92	30	210	16.0	97	99	4,700	2,200	2,700	0.96	87	1.00	NL
2015	Australia	23	0.3	83.5	7.5	85	32	220	17.0	96	99	4,800	2,300	2,800	0.97	88	1.00	AU
2015	Israel	7.5	0.2	82.5	10.5	75	38	230	18.0	95	99	4,900	2,400	2,900	0.98	89	1.00	IL
2015	Switzerland	4.5	0.2	83.5	6.5	89	39	240	19.0	98	99	5,000	2,500	3,000	0.99	90	1.00	CH
2015	Belgium	11	0.2	82.5	8.5	93	31	250	20.0	97	99	5,100	2,600	3,100	0.99	91	1.00	BE
2015	Austria	9	0.2	83.5	7.5	90	33	260	21.0	98	99	5,200	2,700	3,200	1.00	92	1.00	AT
2015	Portugal	11	0.2	82.5	10.5	68	34	270	22.0	96	99	5,300	2,800	3,300	0.99	93	1.00	PT
2015	Finland	5.3	0.2	83.5	6.5	87	35	280	23.0	98	99	5,400	2,900	3,400	1.00	94	1.00	FI
2015	South Africa	25	0.2	64.5	24.5	60	18	290	24.0	65	85	1,500	600	800	0.68	60	0.75	ZA
2015	Brazil	207	2.0	74.5	27.5	51	12	300	25.0	60	80	1,200	500	700	0.62	58	0.70	BR
2015	Russia	143	1.5	73.5	20.5	74	1											

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Year	Country	Population (millions)	GDP (billion USD)	Life expectancy (years)	Infant mortality (per 1,000 live births)	Urban population (%)	Renewable energy (%)	Internet usage (%)	Gender inequality index
2010	USA	310	14,500	78	12	80	10	75	0.25
2011	USA	312	15,000	78	11	81	11	76	0.25
2012	USA	314	15,500	78	11	82	12	77	0.25
2013	USA	316	16,000	78	11	83	13	78	0.25
2014	USA	318	16,500	78	11	84	14	79	0.25
2015	USA	320	17,000	78	11	85	15	80	0.25
2016	USA	322	17,500	78	11	86	16	81	0.25
2017	USA	324	18,000	78	11	87	17	82	0.25
2018	USA	326	18,500	78	11	88	18	83	0.25
2019	USA	328	19,000	78	11	89	19	84	0.25
2020	USA	330	19,500	78	11	90	20	85	0.25
2010	China	1,370	5,900	73	60	50	5	15	0.75
2011	China	1,375	6,200	73	58	51	6	16	0.75
2012	China	1,380	6,500	73	56	52	7	17	0.75
2013	China	1,385	6,800	73	54	53	8	18	0.75
2014	China	1,390	7,100	73	52	54	9	19	0.75
2015	China	1,395	7,400	73	50	55	10	20	0.75
2016	China	1,400	7,700	73	48	56	11	21	0.75
2017	China	1,405	8,000	73	46	57	12	22	0.75
2018	China	1,410	8,300	73	44	58	13	23	0.75
2019	China	1,415	8,600	73	42	59	14	24	0.75
2020	China	1,420	8,900	73	40	60	15	25	0.75
2010	India	1,100	1,800	67	110	30	2	10	0.85
2011	India	1,110	1,900	67	105	31	3	11	0.85
2012	India	1,120	2,000	67	100	32	4	12	0.85
2013	India	1,130	2,100	67	95	33	5	13	0.85
2014	India	1,140	2,200	67	90	34	6	14	0.85
2015	India	1,150	2,300	67	85	35	7	15	0.85
2016	India	1,160	2,400	67	80	36	8	16	0.85
2017	India	1,170	2,500	67	75	37	9	17	0.85
2018	India	1,180	2,600	67	70	38	10	18	0.85
2019	India	1,190	2,700	67	65	39	11	19	0.85
2020	India	1,200	2,800	67	60	40	12	20	0.85
2010	Germany	82	3,500	80	7	90	25	60	0.15
2011	Germany	82	3,600	80	7	90	26	61	0.15
2012	Germany	82	3,700	80	7	90	27	62	0.15
2013	Germany	82	3,800	80	7	90	28	63	0.15
2014	Germany	82	3,900	80	7	90	29	64	0.15
2015	Germany	82	4,000	80	7	90	30	65	0.15
2016	Germany	82	4,100	80	7	90	31	66	0.15
2017	Germany	82	4,200	80	7	90	32	67	0.15
2018	Germany	82	4,300	80	7	90	33	68	0.15
2019	Germany	82	4,400	80	7	90	34	69	0.15
2020	Germany	82	4,500	80	7	90	35	70	0.15
2010	Japan	127	5,400	83	5	95	20	80	0.10
2011	Japan	127	5,400	83	5	95	20	80	0.10
2012	Japan	127	5,400	83	5	95	20	80	0.10
2013	Japan	127	5,400	83	5	95	20	80	0.10
2014	Japan								

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1. The first step in the process of creating a new product is to identify a market need. This involves conducting market research to understand the preferences and behaviors of potential customers. Once a need is identified, the next step is to develop a concept that addresses this need. This concept should be unique, valuable, and feasible. The third step is to create a prototype, which is a preliminary model of the product. This allows the team to test the concept and make necessary adjustments. The fourth step is to conduct a feasibility study, which assesses the technical, financial, and operational viability of the product. Finally, the product is launched into the market, and the team monitors its performance and customer feedback to make further improvements.

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